

## Inkjet Recording Ink Set

### FIELD OF THE INVENTION

The present invention relates to an inkjet recording ink capable of providing an image having excellent preservability and high image quality and also relates to an ink set containing the ink.

### BACKGROUND OF THE INVENTION

With the recent popularization of computers, an inkjet printer is widely used for printing letters or an image on paper, film, cloth or the like not only at offices but also at homes.

The inkjet recording method includes a system of jetting out a liquid droplet by applying a pressure using a piezoelectric element, a system of jetting out a liquid droplet by generating a bubble in an ink under heat, a system of using an ultrasonic wave, and a system of ejecting a liquid droplet by drawing with an electrostatic force. The ink composition used for such inkjet recording includes an aqueous ink, an oily ink and a solid (fusion-type) ink. Among these inks, the aqueous ink becomes mainstream in view of production, handleability, odor, safety and the like.

The coloring agent used in such an ink for inkjet recording method is required to have high solubility in a

solvent, enable high-density recording, provide good color hue, exhibit excellent fastness to light, heat, air, water and chemicals, ensure good fixing property and less bleeding on an image-receiving material, provide an ink having excellent storability, show no toxicity, have high purity, and be available at a low cost. However, it is very difficult to find out a coloring agent satisfying these requirements in a high level.

Various dyes and pigments for inkjet recording method have been already proposed and actually used, however, a coloring agent satisfying all requirements is not yet found out at present. Conventionally well-known dyes and pigments having a Colour Index (C.I.) number can hardly satisfy both color hue and fastness required of the ink for inkjet recording method. Heretofore, studies have been made on a dye having good color hue and fastness with an attempt to develop a dye excellent as the coloring agent for inkjet recording. Particularly, a dye having good color hue and excellent fastness to ozone is highly desired.

On the other hand, many dyes are difficult to dissolve in water and readily precipitate, and it has been found that a problem in that when printed, an abnormal printed part (a failure in that a bronze part, i.e., a matted surface is formed as compared with a normal printed part) resulting from aggregation of dye in a high-density

printed part is produced to deteriorate the image quality. The bronze part is readily generated particularly in a multicolor mixed part.

A method of increasing an amount of a water-soluble organic solvent used so as to prevent the precipitation of dye is not preferred, because the ejection property is worsened due to increase in the viscosity and the light fastness also tends to be worsened. A method of using a dye having high light absorbance in a low concentration may be considered, but a dye also satisfying other performances is difficult to find out in view of technique.

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide an inkjet recording ink set which can provide an image having high image quality and excellent weather resistance such as light fastness, heat fastness and ozone fastness and which hardly causes precipitation even when the inks printed are mixed, and thus prevents the generation of bronze part.

Other objects of the present invention will become apparent from the following description.

The objects of the present invention can be attained by the following techniques.

(1) An inkjet recording ink set comprising at least two inks, wherein each of the inks contains at least one dye having an anionic group, and even when any two inks in

the ink set are mixed, precipitation of the dye does not occur. The precipitation is preferably judged by the presence or absence of precipitation through a microscope when two inks are simultaneously mixed at 25°C and 50% RH (relative humidity), 0.2 ml of the mixed ink is dropped on a glass-made Sekisui Microscope Plate UR-157 (produced by Sekisui Chemical Co., Ltd.) and the plate is allowed to stand at 25°C and 50% RH for 3 days.

(2) An inkjet recording ink set comprising at least three inks, wherein each of the inks contains at least one dye having an anionic group, and even when any three inks in the ink set are mixed, precipitation of the dye does not occur. The precipitation is preferably judged by the presence or absence of precipitation through a microscope when three inks are simultaneously mixed at 25°C and 50% RH (relative humidity), 0.2 ml of the mixed ink is dropped on glass-made Sekisui Microscope Plate UR-157 (produced by Sekisui Chemical Co., Ltd.) and the plate is allowed to stand at 25°C and 50% RH for 3 days.

(3) The inkjet recording ink set as described in (1) or (2), wherein the ink set is an ink set containing yellow, magenta, cyan and black ink compositions.

(4) The inkjet recording ink set as described in any one of (1) to (3), wherein a counter cation of the dye having an anionic group is selected from lithium, sodium,



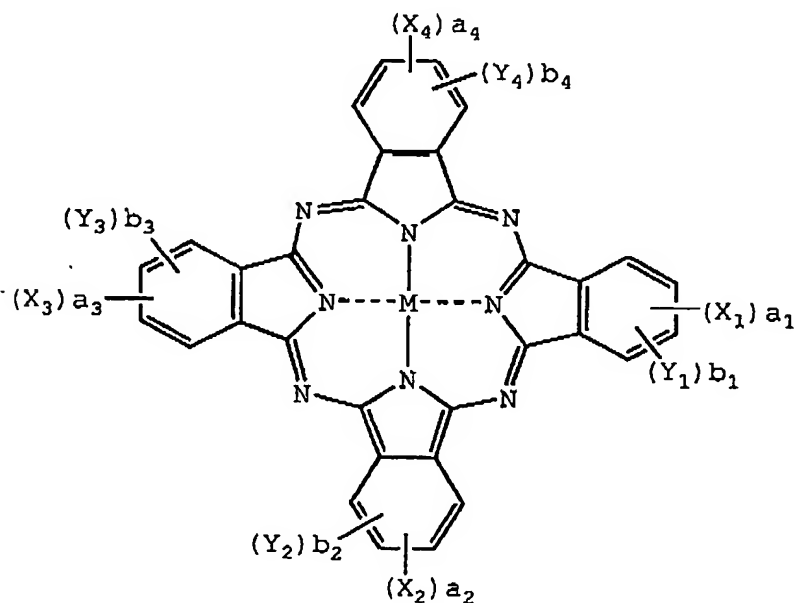
potassium and ammonium.

(5) The inkjet recording ink set as described in any one of (1) to (4), wherein a counter cation of the dye having an anionic group is the same in at least two inks.

(6) The inkjet recording ink set as described in any one of (1) to (5), wherein at least one dye of the dyes having an anionic group has an oxidation potential more positive than 1.0 V (vs SCE).

(7) The inkjet recording ink set as described in any one of (1) to (6), wherein at least one dye of the dyes having an anionic group is represented by any one of the following formulae (CI), (MI), (YI) and (BkI):

Formula (CI):



wherein  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  each independently represents  $-SO-$

, Z,  $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}\text{O}_2\text{-Z}$ ,  $\text{-SO}_2\text{NR}_{1c}\text{R}_{2c}$ , a sulfo group,  $\text{-CONR}_{1c}\text{R}_{2c}$  or  $\text{-CO}_2\text{R}_{1c}$ ,

Z independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group,

$\text{R}_{1c}$  and  $\text{R}_{2c}$  each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group,

provided that when a plurality of Zs are present, the Zs may be the same or different,

$\text{Y}_1$ ,  $\text{Y}_2$ ,  $\text{Y}_3$  and  $\text{Y}_4$  each independently represents a monovalent substituent,

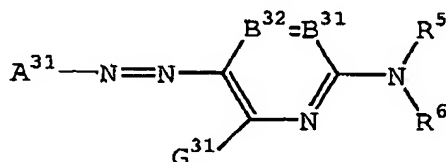
provided that when a plurality of substituents  $\text{X}_1$ ,  $\text{X}_2$ ,  $\text{X}_3$ ,  $\text{X}_4$ ,  $\text{Y}_1$ ,  $\text{Y}_2$ ,  $\text{Y}_3$  or  $\text{Y}_4$  are present, the  $\text{X}_1\text{s}$ ,  $\text{X}_2\text{s}$ ,  $\text{X}_3\text{s}$ ,  $\text{X}_4\text{s}$ ,  $\text{Y}_1\text{s}$ ,  $\text{Y}_2\text{s}$ ,  $\text{Y}_3\text{s}$  or  $\text{Y}_4\text{s}$  may be the same or different,

$a_1$  to  $a_4$  and  $b_1$  to  $b_4$  represent the number of substituents  $\text{X}_1$  to  $\text{X}_4$  and  $\text{Y}_1$  to  $\text{Y}_4$ , respectively,  $a_1$  to  $a_4$  each independently represents an integer of 0 to 4 but all are not 0 at the same time,  $b_1$  to  $b_4$  each independently

represents an integer of 0 to 4, and

M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof;

Formula (MI):



wherein A<sup>31</sup> represents a 5-membered heterocyclic group;

B<sup>31</sup> and B<sup>32</sup> each represents =CR<sup>1</sup>- or -CR<sup>2</sup>=, or one of B<sup>31</sup> and B<sup>32</sup> represents a nitrogen atom and the other represents =CR<sup>1</sup>- or -CR<sup>2</sup>=,

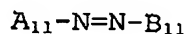
R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, the hydrogen atom of each substituent may be substituted,

G<sup>31</sup>, R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a

carbamoyl group, an alkoxycarbonyl group, an aryloxy-carbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxy carbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxy-carbonylamino group, an aryloxy carbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, the hydrogen atom of each substituent may be substituted, and

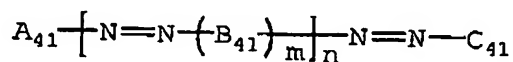
$R^1$  and  $R^5$ , or  $R^5$  and  $R^6$  may combine to form a 5- or 6-membered ring;

Formula (Y1):



wherein  $A_{11}$  and  $B_{11}$  each independently represents a heterocyclic group which may be substituted;

Formula (BK1):



wherein  $A_{41}$ ,  $B_{41}$  and  $C_{41}$  each independently represents an aromatic group which may be substituted or a heterocyclic group which may be substituted ( $A_{41}$  and  $C_{41}$  each is a monovalent group and  $B_{41}$  is a divalent group),  $m$  represents 1 or 2, and  $n$  represents an integer of 0 or more.

(8) The inkjet recording ink set as described in (1), wherein at least one dye of the dyes having an anionic group is a dye having at least two heterocyclic groups.

(9) The inkjet recording ink set as described in (8), wherein at least one of the heterocyclic groups is a 5-membered or 6-membered heterocyclic group containing at least one hetero atom selected from a nitrogen atom, an oxygen atom and a sulfur atom.

(10) The inkjet recording ink set as described in (9), wherein the heterocyclic group contains at least one heterocyclic ring selected from pyridine, thiophene, thiazole, benzothiazole, benzoxazole and furan.

(11) An inkjet recording method using the inkjet recording ink set described in any one of (1) to (10).

(12) An inkjet recording method comprising ejecting an ink droplet according to a recording signal on an image-receiving material to record an image on the image-receiving material comprising a support having thereon an image-receiving layer containing a white inorganic pigment particle, wherein the ink droplet comprises the ink of the

inkjet recording ink set described in (1) to (10).

#### DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, an inkjet recording ink set using an aqueous ink advantageous in view of handleability, odor, safety and the like can be obtained, which provides an image having high image quality and excellent weather resistance such as light fastness, heat fastness and ozone fastness and hardly causes precipitation even when the printed inks are mixed, and thus prevents the generation of a bronze part. In particular, an ink set hardly generating a bronze part in the portion where a cyan dye and a magenta dye are printed (for example, a blue area), hardly causing clogging of nozzle and providing an excellent recorded image with high density, can be provided.

The present invention is described in detail below.

The present invention is an inkjet recording ink set comprising at least two inks, wherein the ink contains at least one dye having an anionic group and even when any two (any three or more) inks in the ink set are selected and mixed, precipitation of THE dye does not occur. The precipitation is judged in the following manner. Specifically, two (or three or more) inks are simultaneously mixed at room temperature (25°C) and a relative humidity of 50% RH, 0.2 ml of the mixed ink is dropped on glass-made Sekisui Microscope Plate UR-157

(produced by Sekisui Chemical Co., Ltd.), the plate is allowed to stand at room temperature for 3 days, and then the presence or absence of precipitation is determined through a microscope.

Examples of the anionic group in the dye having an anionic group include a sulfo group, a carboxyl group and a phosphono group. The anionic group is preferably a carboxyl group, a phosphono group or a sulfo group, more preferably a carboxyl group or a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include an ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, the cations described below are preferred.

As for the number of anionic groups, the dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule. The "anionic group" is a subordinate concept of an "ionic hydrophilic group" described later.

The cation contained in the inkjet recording ink of the present invention is preferably a monovalent metal ion, a hydrogen ion, an ammonium ion, an organic quaternary nitrogen ion or an ion produced by addition of a proton to

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a nitrogen atom in a basic organic material (hereinafter, referred to as a "cation of the present invention").

Examples of the monovalent metal ion include lithium ion, potassium ion, sodium ion and cesium ion.

Examples of the organic quaternary nitrogen ion include tetramethylammonium ion, tetraethylammonium ion, tetrabutylammonium ion, benzyltrimethylammonium ion, benzyltributylammonium ion, cetylpyridinium ion, cetyltrimethylammonium ion, N,N'-dimethylpiperidinium ion and N,N'-dimethylimidazolium ion.

The nitrogen atom in a basic organic material indicates a nitrogen atom contained, for example, in trimethylamine, triethylamine, triethanolamine, methylamine, dimethylamine, butylamine, dibutylamine, piperidine, morpholine, piperazine, pyrrolidine, N-methylpiperidine, N-methylmorpholine, pyridine, quinoline, pyrazine, pyrimidine, pyrazole or imidazole.

Among these, from the standpoint of enhancing the water solubility of the dye having an anionic group, preferred as the cation component contained in the ink are lithium ion, potassium ion, sodium ion and ammonium ion, which can make the molecular weight small, more preferred is lithium ion.

In each ink for use in the present invention it is preferred that the total amount of cations other than the



above-described cation is 0.5 wt% or less in the ink.

Examples of the cation other than the above-described cation include magnesium ion, zinc ion, calcium ion, strontium ion, aluminum ion and transition metal ion.

When the total amount of such cations in the ink increases, the dye may undesirably tend to precipitate in the ink or in the printing part. Thus, the total amount of such cations is preferably 0.5 wt% or less and more preferably 0.1 wt% or less.

The ion component in the ink is mainly originated in the counter ion of the ionic group of the dye or additives such as surfactant, pH adjusting agent and antiseptic, and by appropriately selecting the kind and amount of the counter ion of the dye or additives, the amount of cation can be adjusted.

The above-described dye is preferably a dye having an oxidation potential more positive than 1.0 V (vs SCE).

As the above-described dye, magenta dyes described in JP-A-2002-371214 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), phthalocyanine dyes described in JP-A-2002-309118, and water-soluble phthalocyanine dyes described in JP-A-2003-12952 and JP-A-2003-12956 are preferably used. Preferred cyan dye, magenta dye, yellow dye and black dye are described in detail below.

. [Cyan Dye]

The present inventors have made intensive investigations on the inkjet recording ink and found that the properties required of the dye are 1) to give a good color hue and be free of change in the color hue (solvate), 2) to exhibit excellent fastness (to light, ozone, NOx, solvent, oil and water), 3) to be safe (not carcinogenic by AMES test, not irritating to skin and easily degradable), 4) to be inexpensive, 5) to have high  $\epsilon$ , 6) to be highly soluble, and 7) to have strong fixing property to media.

The properties required of the ink and conc. ink are 1) to be uniform irrespective of the temperature and aging, 2) to be less contaminated, 3) to exhibit good permeation to media, 4) to be uniform in the hitting size, 5) to be usable for all types of paper, 6) to be easily prepared, 7) to ensure no ejection error, less bubbling and easy defoaming, and 8) to be stably ejected.

The properties required of the image is 1) to be clear without bleeding, discoloration and beading, 2) to have scratch resistance, 3) to have high and uniform gloss, 4) to have good image preservability and excellent balance in color fading, 5) to be quickly dried, 6) to be printed at a high speed, and 7) to have no image density dependency in the color fading ratio.

The properties required of the inkjet recording ink

is to be excellent in both light fastness and ozone resistance and small in the change of color hue and surface state (less generation of bronze and less precipitation of dye). With respect to the light fastness (OD1.0), the light fastness with TAC filter on Epson PM Photographic Image-Receiving Paper under Xe of 1.1 W/m (intermittent condition) is preferably 90% or more in terms of the residual color ratio for 3 days. Also, the dye residual ratio for 14 days is preferably 85% or more. With respect to the ozone resistance, the ozone resistance (OD1.0) under condition of 5 ppm or less of ozone is preferably 60% or more, more preferably 70% or more, still more preferably 80% or more, in terms of the dye residual ratio for one day. Also, the dye residual ratio for 5 days is preferably 25% or more, more preferably 40% or more, still more preferably 50% or more. Samples varied in the amount of the dye coated are prepared by GTC and the amount of Cu element contained in the dye is measured by a fluorescent X ray.

The Cu ion is present in the form of a phthalate as a result of decomposition of a phthalocyanine dye. The amount of the salt present in an actual print is preferably 10 mg/m<sup>2</sup> or less in terms of Cu ion. The amount of Cu flowed out from the print is determined by forming an entire cyan solid image having a phthalate amount of 20 mg/m<sup>2</sup> or less in terms of Cu ion, discoloring the image

with ozone and analyzing the amount of ion flowed out into water. All Cu compounds are trapped by the image-receiving material before the discoloration. The amount of ion flowed out into water is preferably 20% or less of all dyes.

It has been found by the present invention that a phthalocyanine dye having such properties can be obtained, for example, by 1) elevating the oxidation potential, 2) enhancing the aggregation property, 3) introducing an aggregation accelerating group, intensifying the hydrogen bond at the time of  $\pi$ - $\pi$  stacking or 4) not incorporating a substituent at the  $\alpha$ -position, that is, facilitating the stacking.

Conventional phthalocyanine dyes used for inkjet ink are derived from an unsubstituted phthalocyanine through sulfonation and these are a mixture which cannot be specified in the number and positions of substituents. On the other hand, the dye preferably used in the inkjet recording ink of the present invention is a phthalocyanine dye which can be specified in the number and positions of substituents. The first structural feature is that the dye is a water-soluble phthalocyanine dye obtained by not passing through sulfonation of an unsubstituted phthalocyanine. The second structural feature is that the dye has an electron-withdrawing group at the  $\beta$ -position of a benzene ring of phthalocyanine, preferably at the  $\beta$ -

positions of all benzene rings. Specifically, useful dyes are those where a sulfonyl group is substituted (see, JP-A-2002-249677 and JP-A-2003-119415), a sulfamoyl group in general is substituted (see, JP-A-2002-302623 and JP-A-2003-3109), a heterocyclic sulfamoyl group is substituted (see, JP-A-2002-294097 and JP-A-2003-3086), a heterocyclic sulfonyl group is substituted (see, JP-A-2002-275386 and JP-A-2003-3099), a specific sulfamoyl group is substituted (see, JP-A-2002-256167), a carbonyl group is substituted (see, JP-A-2003-213153), or a specific substituent for enhancing the solubility or ink stability or preventing the bronzing, such as substituent having an asymmetric carbon (see, JP-A-2003-213168) or Li salt (see, JP-A-2003-213167) is substituted.

The first physical feature of the dye preferably used in the inkjet recording ink of the present invention is to have a high oxidation potential. The oxidation potential is preferably more positive than 1.00 V, more preferably more positive than 1.1 V, and most preferably more positive than 1.15 V. The second physical feature is to have a strong aggregation property. Specifically, the dye having such a property includes those where the aggregation of oil-soluble dyes is specified (see, JP-A-2001-342373) or the aggregation of water-soluble dyes is specified (see, JP-A-2002-309118).

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With respect to the relationship between the number of aggregation accelerating groups and the performance (light absorbance of ink), when the aggregation accelerating group is introduced, reduction of light absorbance or shifting of  $\lambda_{\max}$  to the shorter wave is liable to occur even in a dilute solution. With respect to the relationship between the number of aggregation accelerating groups and the performance (reflection OD on Epson PM920 Image-Receiving Paper), as the number of aggregation accelerating groups increases, the reflection OD at the same ion intensity more decreases. That is, the aggregation is considered to proceed on the image-receiving paper. With respect to the relationship between the number of aggregation accelerating groups and the performance (ozone resistance/light fastness), as the number of aggregation accelerating groups increases, the ozone resistance is more enhanced. A dye having a large number of aggregation accelerating groups tends to be enhanced also in the light fastness. In order to impart the ozone resistance, the above-described substituents corresponding to  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  are desirably present. The reflection OD and the fastness are in the trade-off relationship and therefore, it is necessary to enhance the light fastness without weakening the aggregation.

Preferred embodiments of the ink of the present

invention are:

1) a cyan ink where the light fastness with TAC filter on Epson PM Photographic Image-Receiving Paper under Xe of 1.1 W/m (intermittent condition) is 90% or more in terms of the residual color ratio for 3 days;

2) a cyan ink where after storage of a monochromatic portion printed by using a monochrome (cyan) ink to give a cyan reflection density of 0.9 to 1.1 through a Status A filter in an ozone environment of 5 ppm for 24 hours has a dye residual ratio (density after discoloration/initial density $\times$ 100) of 60% (preferably 80%) or more;

3) a cyan ink where after ozone discoloration under the same conditions as in 2, the amount of Cu ion flowed out into water is 20% or less of all dyes; and

4) a cyan ink having permeability such that the amount of ink permeated into a specific image-receiving paper is 30% or more of the upper portion of the image-receiving layer.

The dye contained in the cyan inkjet recording ink of the present invention is favourably a phthalocyanine dye, preferably a water-soluble dye having an oxidation potential more positive than 1.0, more preferably a dye having ozone gas fastness satisfying the above-described conditions, still more preferably the phthalocyanine dye

represented by formula (CI) above.

The phthalocyanine dye is a dye having good fastness but it is known to be inferior in the fastness to ozone gas when used as a dye for inkjet recording.

In the present invention, an electron-withdrawing group is preferably introduced into the phthalocyanine skeleton to render the oxidation potential more positive than 1.0 V (vs SCE) and thereby reduce the reactivity with ozone which is an electrophilic agent. A more positive oxidation potential is more preferred and the oxidation potential is more preferably more positive than 1.1 V (vs SCE) and most preferably more positive than 1.15 V (vs SCE).

The oxidation potential value ( $E_{ox}$ ) can be easily measured by one skilled in the art and the method therefor is described, for example, in P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers (1954), A.J. Bard et al., Electrochemical Methods, John Wiley & Sons (1980), and Akira Fujishima et al., Denkikagaku Sokutei Ho (Electrochemical Measuring Methods), Gihodo Shuppan Sha (1984).

More specifically, a test sample is dissolved at a concentration of  $1 \times 10^{-2}$  to  $1 \times 10^{-6}$  mol/liter in a solvent such as dimethylformamide or acetonitrile containing a supporting electrolyte such as sodium perchlorate or tetrapropylammonium perchlorate and the oxidation potential



is measured as a value to SCE (saturated calomel electrode) by using a cyclic voltammetry, a direct current polarography or the like. The value sometimes deviates on the order of several tens of millivolts due to the effect of liquid junction potential, liquid resistance of sample solution, or the like, however, reproducibility of the potential can be guaranteed by using a standard sample (for example, hydroquinone).

In order to univocally specify the potential, in the present invention, a value (vs SCE) measured in a dimethylformamide (concentration of dye:  $0.001 \text{ mol dm}^{-3}$ ) containing  $0.1 \text{ mol dm}^{-3}$  of tetrapropylammonium perchlorate as the supporting electrolyte is used as the oxidation potential of the dye.

The  $E_{ox}$  (oxidation potential) value indicates the transferability of an electron from the sample to the electrode and as the value is larger (the oxidation potential is more positive), the electron is less transferable from the sample to the electrode, in other words, the oxidation less occurs. As for the relationship with the structure of compound, the oxidation potential becomes more positive when an electron-withdrawing group is introduced, and becomes more negative when an electron-donating group is introduced. In the present invention, the oxidation potential is preferably rendered more

positive by introducing an electron-withdrawing group into the phthalocyanine skeleton so as to reduce the reactivity with ozone which is an electrophilic agent. When the Hammett's substituent constant  $\sigma_p$  value as a measure for the electron-withdrawing property or electron-donating property of substituent is used, the oxidation potential can be rendered more positive by introducing a substituent having a large  $\sigma_p$  value, such as sulfinyl group, sulfonyl group or sulfamoyl group.

Also for the purpose of such potential control, the phthalocyanine dye represented by formula (CI) above is preferably used.

The phthalocyanine dye having the above-described oxidation potential is apparently a cyan dye excellent in both the light fastness and the ozone resistance, because the dye satisfies those conditions for light fastness and ozone resistance.

The phthalocyanine dye (preferably the phthalocyanine dye represented by formula (CI)) for use in the present invention is described in detail below.

In formula (CI),  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  each independently represents  $-\text{SO}-Z$ ,  $-\text{SO}_2-Z$ ,  $-\text{SO}_2\text{NR}_{1c}\text{R}_{2c}$ , a sulfo group,  $-\text{CONR}_{1c}\text{R}_{2c}$  or  $-\text{CO}_2\text{R}_{1c}$ . Among these substituents, preferred are  $-\text{SO}-Z$ ,  $-\text{SO}_2-Z$ ,  $-\text{SO}_2\text{NR}_{1c}\text{R}_{2c}$  and  $-\text{CONR}_{1c}\text{R}_{2c}$ , more preferred are  $-\text{SO}_2-Z$  and  $-\text{SO}_2\text{NR}_{1c}\text{R}_{2c}$ , and most preferred is -

$\text{SO}_2\text{-Z}$ . In the case where  $a_1$  to  $a_4$ , showing the number of substituents each represents a number of 2 or more, a plurality of substituents  $X_1$ ,  $X_2$ ,  $X_3$  or  $X_4$  may be the same or different and each independently represents any one of the above-described groups.  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  all are  $\text{-SO}_2\text{-Z}$  and  $Z$ s are different from each other, or may include substituents different from each other, for example,  $\text{-SO}_2\text{-Z}$  and  $\text{-SO}_2\text{NR}_{1c}\text{R}_{2c}$ .

Each  $Z$  independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group.

$R_{1c}$  and  $R_{2c}$  each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a

substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, more preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that both  $R_{1c}$  and  $R_{2c}$  are hydrogen atoms.

The substituted or unsubstituted alkyl group represented by  $R_{1c}$ ,  $R_{2c}$  or  $Z$  is preferably an alkyl group having from 1 to 30 carbon atoms, more preferably a branched alkyl group because the solubility of dye and the stability of ink are improved, still more preferably an alkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when  $Z$ ,  $R_{1c}$ ,  $R_{2c}$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregation property and fastness of dye are improved. Further, the alkyl group may be substituted by a halogen atom or an ionic hydrophilic group. The number of carbon atoms in the alkyl group does not contain carbon atoms of

substituents and this applies to other groups also.

The substituted or unsubstituted cycloalkyl group represented by  $R_{1c}$ ,  $R_{2c}$  or  $Z$  is preferably a cycloalkyl group having from 5 to 30 carbon atoms, more preferably a cycloalkyl group having an asymmetric carbon (use in the racemic form) because the solubility of dye and the stability of ink are improved. Examples of the substituent include those described later as the substituent when  $Z$ ,  $R_{1c}$ ,  $R_{2c}$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregation property and fastness of dye are enhanced. Further, the cycloalkyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted alkenyl group represented by  $R_{1c}$ ,  $R_{2c}$  or  $Z$  is preferably an alkenyl group having from 2 to 30 carbon atoms, more preferably a branched alkenyl group because the solubility of dye and the stability of ink are improved, still more preferably an alkenyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when  $Z$ ,  $R_{1c}$ ,  $R_{2c}$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano

group, an amido group and a sulfonamido group are preferred because the aggregation property and fastness of dye are enhanced. Further, the alkenyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted aralkyl group represented by  $R_{1c}$ ,  $R_{2c}$  or  $Z$  is preferably an aralkyl group having from 7 to 30 carbon atoms, more preferably a branched aralkyl group because the solubility of dye and the stability of ink are improved, still more preferably an aralkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when  $Z$ ,  $R_{1c}$ ,  $R_{2c}$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregation property and fastness of dye are enhanced. Further, the aralkyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted aryl group represented by  $R_{1c}$ ,  $R_{2c}$  or  $Z$  is preferably an aryl group having from 6 to 30 carbon atoms. Examples of the substituent include those described later as the substituent when  $Z$ ,  $R_{1c}$ ,  $R_{2c}$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  further have a substituent. In particular, an electron-withdrawing group is preferred because the dye can have a more positive

oxidation potential and be improved in the fastness. Examples of the electron-withdrawing group include those having a positive Hammett's substituent constant  $\sigma_p$  value. Among these, preferred are a halogen atom, a heterocyclic group, a cyano group, a carboxyl group, an acylamino group, a sulfonamido group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group, more preferred are a cyano group, a carboxyl group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group.

The heterocyclic group represented by  $R_{1c}$ ,  $R_{2c}$  or  $Z$  is preferably a 5- or 6-membered ring and the ring may be further condensed. Also, the heterocyclic group may be an aromatic heterocyclic group or a non-aromatic heterocyclic group. Examples of the heterocyclic group represented by  $R_{1c}$ ,  $R_{2c}$  and  $Z$  are shown below in the form of a heterocyclic ring by omitting the substitution site. The substitution site is not limited and, for example, in the case of pyridine, the 2-position, 3-position and 4-position can be substituted. Examples of the heterocyclic ring include pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, pyrrole, indole, furan, benzofuran, thiophene, benzothiophene, pyrazole, imidazole,

benzimidazole, triazole, oxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, thiadiazole, isoxazole, benzisoxazole, pyrrolidine, piperidine, piperazine, imidazolidine and thiazoline. In particular, an aromatic heterocyclic group is preferred. Preferred examples thereof include, shown in the same manner as above, pyridine, pyrazine, pyrimidine, pyridazine, triazine, pyrazole, imidazole, benzimidazole, triazole, thiazole, benzothiazole, isothiazole, benzisothiazole and thiadiazole. The groups each may have a substituent and examples of the substituent include those described later as the substituent when Z, R<sub>1c</sub>, R<sub>2c</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> further have a substituent. Preferred substituents are the same as the above-described substituents of the aryl group and more preferred substituents are the same as the above-described more preferred substituents of the aryl group.

Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> each independently represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, an amino group, an alkylamino group, an alkoxy group, an aryloxy group, an acylamino group, an arylamino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a



, sulfonyl group, an alkoxy carbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxy carbonyl group, an aryloxy carbonylamino group, an imido group, a heterocyclic thio group, a phosphoryl group, an acyl group, a carboxyl group or a sulfo group. The groups each may further have a substituent.

$Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  each is preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

When  $Z$ ,  $R_{1c}$ ,  $R_{2c}$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  each is a group which can further have a substituent, the group may further have the following substituents.

Examples of the substituent include a linear or branched alkyl group having from 1 to 12 carbon atoms, a linear or branched aralkyl group having from 7 to 18 carbon atoms, a linear or branched alkenyl group having from 2 to 12 carbon atoms, a linear or branched alkynyl group having from 2 to 12 carbon atoms, a linear or branched cycloalkyl group having from 3 to 12 carbon atoms, a linear or

branched cycloalkenyl group having from 3 to 12 carbon atoms (these groups each is preferably a group having a branched chain because the solubility of dye and the stability of ink are improved, more preferably a group having an asymmetric carbon; specific examples of the groups include a methyl group, an ethyl group, a propyl group, an isopropyl group, a sec-butyl group, a tert-butyl group, a 2-ethylhexyl group, a 2-methylsulfonylethyl group, a 3-phenoxypropyl group, a trifluoromethyl group, a cyclopentyl group, a halogen atom (e.g., chlorine, bromine), an aryl group (e.g., phenyl, 4-tert-butylphenyl, 2,4-di-tert-amylphenyl), a heterocyclic group (e.g., imidazolyl, pyrazolyl, triazolyl, 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl), a cyano group, a hydroxyl group, a nitro group, a carboxy group, an amino group, an alkyloxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-methanesulfonylethoxy), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, 4-tert-butylphenoxy, 3-nitrophenoxy, 3-tert-butyloxycarbamoylphenoxy, 3-methoxycarbamoyl), an acylamino group (e.g., acetamido, benzamido, 4-(3-tert-butyl-4-hydroxyphenoxy)butanamido), an alkylamino group (e.g., methylamino, butylamino, diethylamino, methylbutylamino), an anilino group (e.g., phenylamino, 2-chloroanilino), a ureido group (e.g., phenylureido, methylureido, N,N-dibutylureido), a sulfamoylamino group (e.g., N,N-

.dipropylsulfamoylamino), an alkylthio group (e.g., methylthio, octylthio, 2-phenoxyethylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-tert-octylphenylthio, 2-carboxyphenylthio), an alkyloxycarbonylamino group (e.g., methoxycarbonylamino), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido, p-toluenesulfonamido), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-phenylsulfamoyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, toluenesulfonyl), an alkyloxycarbonyl group (e.g., methoxycarbonyl, butyloxycarbonyl), a heterocyclic oxy group (e.g., 1-phenyltetrazol-5-oxy, 2-tetrahydropyranyloxy), an azo group (e.g., phenylazo, 4-methoxyphenylazo, 4-pivaloylaminophenylazo, 2-hydroxy-4-propanoylphenylazo), an acyloxy group (e.g., acetoxy), a carbamoyloxy group (e.g., N-methylcarbamoyloxy, N-phenylcarbamoyloxy), a silyloxy group (e.g., trimethylsilyloxy, dibutylmethylsilyloxy), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino), an imido group (e.g., N-succinimido, N-phthalimido), a heterocyclic thio group (e.g., 2-benzothiazolylthio, 2,4-di-phenoxy-1,3,5-triazole-6-thio, 2-pyridylthio), a sulfinyl group (e.g., 3-phenoxypropylsulfinyl), a phosphonyl group (e.g., phenoxyphosphonyl, octyloxyphosphonyl, phenylphosphonyl), an aryloxycarbonyl

group (e.g., phenoxycarbonyl), an acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl), and an ionic hydrophilic group (e.g., carboxyl, sulfo, phosphono, quaternary ammonium).

In the case where the phthalocyanine dye represented by formula (CI) is water-soluble, the dye preferably contains an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include an ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among the counter ions, alkali metal salts are preferred, and a lithium salt is more preferred because the solubility of dye and the stability of ink are enhanced. The phthalocyanine dye represented by formula (CI) more preferably contains an anionic group and as for the number of anionic groups, the phthalocyanine-base dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, per one molecule.

$a_1$  to  $a_4$  and  $b_1$  to  $b_4$  represent the number of substituents  $X_1$  to  $X_4$  and  $Y_1$  to  $Y_4$ , respectively.  $a_1$  to  $a_4$  each independently represents an integer of 0 to 4 but all are not 0 at the same time.  $b_1$  to  $b_4$  each independently represents an integer of 0 to 4. When  $a_1$  to  $a_4$  and  $b_1$  to  $b_4$  each represents a number of 2 or more, a plurality of substituents  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  or  $Y_4$  may be the same or different.

$a_1$  and  $b_1$  satisfy the relationship of  $a_1+b_1=4$ . In particular, a combination that  $a_1$  represents 1 or 2 and  $b_1$  represents 3 or 2 is preferred, and a combination that  $a_1$  represents 1 and  $b_1$  represents 3 is most preferred.

The same relationship as that between  $a_1$  and  $b_1$  is present in each of the pairs  $a_2$  and  $b_2$ ,  $a_3$  and  $b_3$ , and  $a_4$  and  $b_4$ , and the preferred combination is also the same.

M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof.

M is preferably a hydrogen atom, a metal element such as Li, Na, K, Mg, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Si, Ge, Sn, Pb, Sb and Bi, an oxide such as VO and GeO, a hydroxide such as  $\text{Si(OH)}_2$ ,  $\text{Cr(OH)}_2$  and  $\text{Sn(OH)}_2$ , or a halide such as AlCl,  $\text{SiCl}_2$ , VCl,  $\text{VCl}_2$ , VOCl, FeCl, GaCl and ZrCl, more preferably Cu, Ni, Zn or Al, and most preferably Cu.

. . . Also, Pc (phthalocyanine ring) may form a dimer (for example, Pc-M-L-M-Pc) or a trimer through L (divalent linking group). In such a case, Ms may be the same or different.

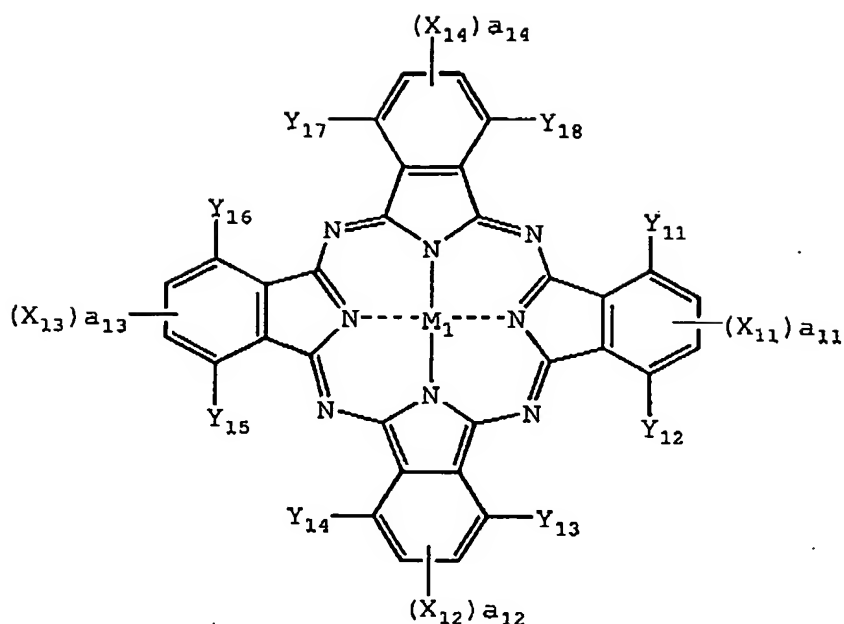
The divalent linking group represented by L is preferably an oxy group -O-, a thio group -S-, a carbonyl group -CO-, a sulfonyl group -SO<sub>2</sub>-, an imino group -NH-, a methylene group -CH<sub>2</sub>- or a group formed by combining two or more of these groups.

As for the preferred combination of substituents in the compound represented by formula (CI), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

Among the phthalocyanine dyes represented by formula (CI), a phthalocyanine dye having a structure represented by formula (CII) is more preferred.

Formula (CII):

Formula (CII):



The phthalocyanine dye represented by formula (CII) of the present invention is described in detail below.

In formula (CII),  $X_{11}$  to  $X_{14}$  and  $Y_{11}$  to  $Y_{18}$  have the same meanings as  $X_1$  to  $X_4$  and  $Y_1$  to  $Y_4$  in formula (CI), respectively, and preferred examples are also the same.  $M_1$  has the same meaning as  $M$  in formula (CI) and preferred examples are also the same.

In formula (CII),  $a_{11}$  to  $a_{14}$  each independently represents an integer of 1 or 2 and preferably satisfy  $4 \leq a_{11} + a_{12} + a_{13} + a_{14} \leq 6$ , and  $a_{11} = a_{12} = a_{13} = a_{14} = 1$  is more preferred.

$X_{11}$ ,  $X_{12}$ ,  $X_{13}$  and  $X_{14}$  may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where  $X_{11}$ ,

$X_{12}$ ,  $X_{13}$  and  $X_{14}$  all are  $-\text{SO}_2-\text{Z}$  and  $\text{Zs}$  are different from each other, or may include substituents different from each other, for example,  $-\text{SO}_2-\text{Z}$  and  $-\text{SO}_2\text{NR}_{1c}\text{R}_{2c}$ .

In the phthalocyanine dye represented by formula (CII), the following combinations of substituents are particularly preferred.

$X_{11}$  to  $X_{14}$  each independently represents preferably  $-\text{SO}-\text{Z}$ ,  $-\text{SO}_2-\text{Z}$ ,  $-\text{SO}_2\text{NR}_{1c}\text{R}_{2c}$  or  $-\text{CONR}_{1c}\text{R}_{2c}$ , more preferably  $-\text{SO}_2-\text{Z}$  or  $-\text{SO}_2\text{NR}_{1c}\text{R}_{2c}$ , and most preferably  $-\text{SO}_2-\text{Z}$ .

Each  $\text{Z}$  independently represents preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregation property and fastness are improved.

$\text{R}_{1c}$  and  $\text{R}_{2c}$  each independently represents preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted



or unsubstituted heterocyclic group, more preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that both  $R_{1c}$  and  $R_{2c}$  are hydrogen atoms. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregation property and fastness are improved.

$Y_{11}$  to  $Y_{18}$  each independently represents preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

$a_{11}$  to  $a_{14}$  each independently represents preferably 1 or 2 and it is more preferred that all are 1.

$M_1$  represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof, preferably Cu, Ni, Zn or Al, and most preferably Cu.

. . . In the case where the phthalocyanine dye represented by formula (CII) is water-soluble, the dye preferably contains an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include an ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among the counter ions, alkali metal salts are preferred and a lithium salt is more preferred because the solubility of dye and the stability of ink are enhanced. The phthalocyanine dye represented by formula (CII) more preferably contains an anionic group and as for the number of anionic groups, the phthalocyanine-base dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, per molecule.

As for the preferred combination of substituents in the compound represented by formula (CII), a compound where at least one of various substituents is the preferred group

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is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

As for the chemical structure of the phthalocyanine dye of the present invention, at least one electron-withdrawing group such as sulfinyl group, sulfonyl group and sulfamoyl group is preferably introduced into respective four benzene rings of phthalocyanine such that the total of  $\sigma_p$  values of the substituents in the entire phthalocyanine skeleton becomes 1.6 or more.

The Hammett's substituent constant  $\sigma_p$  value is briefly described. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a  $\sigma_p$  value and a  $\sigma_m$  value and these values can be found in a large number of ordinary publications and they are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979).

Inevitably in view of the synthesis method, the

phthalocyanine derivative represented by formula (CI) is usually a mixture of analogues different in the site where the substituents  $X_n$  ( $n=1$  to  $4$ ) and  $Y_m$  ( $m=1$  to  $4$ ) are introduced and in the number of the substituents introduced. Accordingly, these analogue mixtures are statistically averaged and represented by a formula in many cases. In the present invention, it has been found that when these analogue mixtures are classified into the following three types, a specific mixture is particularly preferred. The phthalocyanine dye analogue mixtures represented by formulae (CI) and (CII) are defined by classifying these into the following three types based on the substitution site. The positions of  $Y_{11}$ ,  $Y_{12}$ ,  $Y_{13}$ ,  $Y_{14}$ ,  $Y_{15}$ ,  $Y_{16}$ ,  $Y_{17}$ , and  $Y_{18}$  in formula (CII) are designated as 1, 4, 5, 8, 9, 12, 13 and 16, respectively.

(1)  $\beta$ -Position substitution type:

A phthalocyanine dye having specific substituents at the 2- and/or 3-position, the 6- and/or 7-position, the 10- and/or 11-position, and the 14- and/or 15-position.

(2)  $\alpha$ -Position substitution type:

A phthalocyanine dye having specific substituents at the 1- and/or 4-position, the 5- and/or 8-position, the 9- and/or 12-position, and the 13- and/or 16-position.

(3)  $\alpha, \beta$ -Position mixed substitution type:

A phthalocyanine dye having specific substitutions at

the 1- to 16-positions without any regularity.

In the present invention, phthalocyanine dye derivatives different in the structure (particularly in the substitution site) are described by using the  $\beta$ -position substitution type,  $\alpha$ -position substitution type and  $\alpha,\beta$ -position mixed substitution type.

The phthalocyanine derivative for use in the present invention can be synthesized by combining the methods described or cited, for example, in Shirai and Kobayashi, Phthalocyanine -Kagaku to Kino- (Phthalocyanine -Chemistry and Function-), pp. 1-62, IPC, and C.C. Leznoff and A.B.P. Lever, Phthalocyanines - Properties and Applications, pp. 1-54, VCH, or methods analogous thereto.

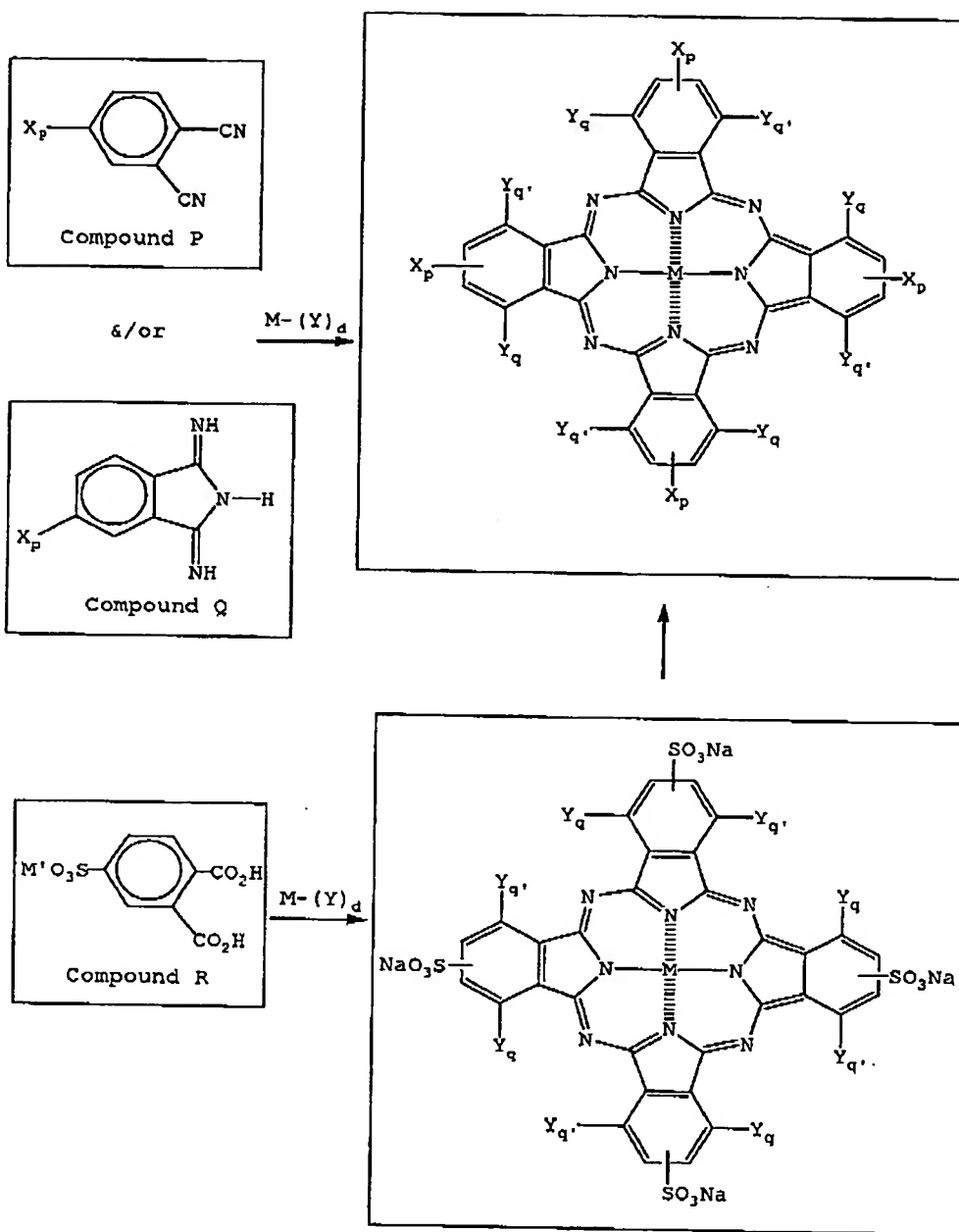
The phthalocyanine compound represented by formula (CI) of the present invention can be synthesized, for example, through sulfonation, sulfonyl chloridation or amidation of an unsubstituted phthalocyanine compound as described in WO 00/17275, WO 00/08103, WO 00/08101 and WO 98/41853 and JP-A-10-36471. In such a case, sulfonation may take place at any site of the phthalocyanine nucleus and the number of sites sulfonated is difficult to control. Accordingly, when a sulfo group is introduced under such reaction conditions, the positions and number of sulfo groups introduced into the product cannot be specified and a mixture of those different in the number of substituents

or in the substitution site inevitably results. If the compound of the present invention is synthesized starting from such a product, the compound of the present invention is obtained as an  $\alpha,\beta$ -position mixed substitution type mixture containing several kinds of compounds different in the number of substituents or in the substitution site because the number of sulfamoyl groups substituted on the heterocyclic ring or their substitution sites cannot be specified.

As described above, for example, when many electron-withdrawing groups such as sulfamoyl group are introduced into the phthalocyanine nucleus, the oxidation potential becomes more positive and the ozone resistance is increased. However, according to the above-described synthesis method, a phthalocyanine dye where the number of electron-withdrawing groups introduced is small, namely, the oxidation potential is more negative, is inevitably mingled. Therefore, in order to improve the ozone resistance, it is preferred to use a synthesis method where the production of a compound having a more negative oxidation potential is suppressed.

The phthalocyanine compound represented by formula (CII) of the present invention can be synthesized, for example, by reacting a phthalonitrile derivative (Compound P) shown below and/or a diiminoisoindoline derivative

• (Compound Q) shown below with a metal derivative represented by formula (CIII) or can be derived from a tetrasulfophthalocyanine compound obtained by reacting a 4-sulfophthalonitrile derivative (Compound R) shown below with a metal derivative represented by formula (CIII).



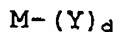
In the formulae above,  $X_p$  corresponds to  $X_{11}$ ,  $X_{12}$ ,  $X_{13}$  or  $X_{14}$  in formula (CII) and  $Y_q$  and  $Y_{q'}$  each corresponds to



$\cdot Y_{11}, Y_{12}, Y_{13}, Y_{14}, Y_{15}, Y_{16}, Y_{17}$  or  $Y_{18}$  in formula (CII). In Compound R,  $M'$  represents a cation.

Examples of the cation represented by  $M'$  include alkali metal ions such as Li, Na and K, and organic cations such as triethylammonium ion and pyridinium ion.

Formula (CIII):

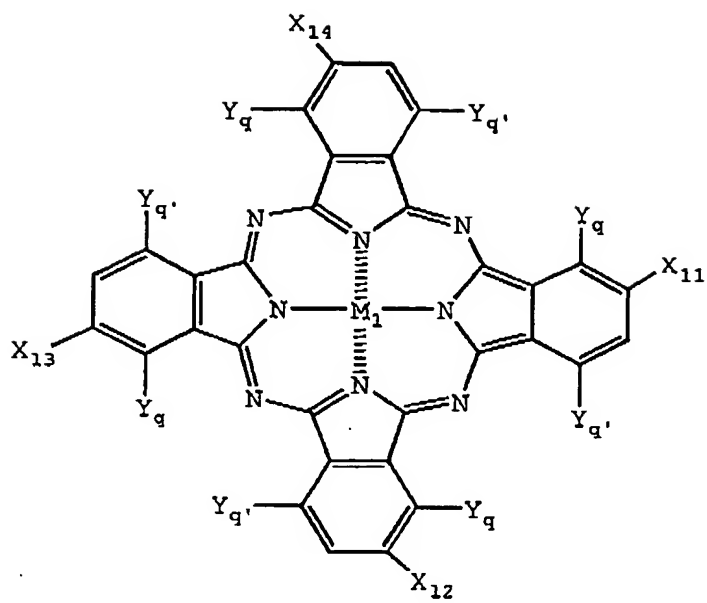


wherein M has the same meaning as M in formulae (CI) and (CII), Y represents a monovalent or divalent ligand such as halogen atom, acetate anion, acetylacetonate and oxygen, and d represents an integer of 1 to 4.

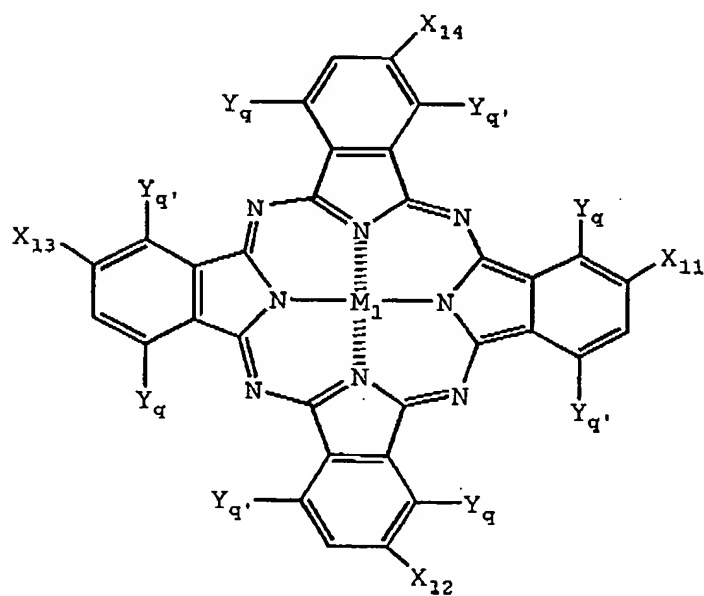
That is, according to the synthesis method described above, a specific number of desired substituents can be introduced. Particularly, in the case of introducing a large number of electron-withdrawing groups so as to render the oxidation potential more positive as in the present invention, the synthesis method is very excellent as compared with the above-described method for synthesizing the phthalocyanine compound of formula (CI).

The thus-obtained phthalocyanine compound represented by formulae (CII) is usually a mixture of compounds represented by the following formulae (a)-1 to (a)-4 which are isomers with respect to the substitution site of each  $X_p$ , namely, the  $\beta$ -position substitution type.

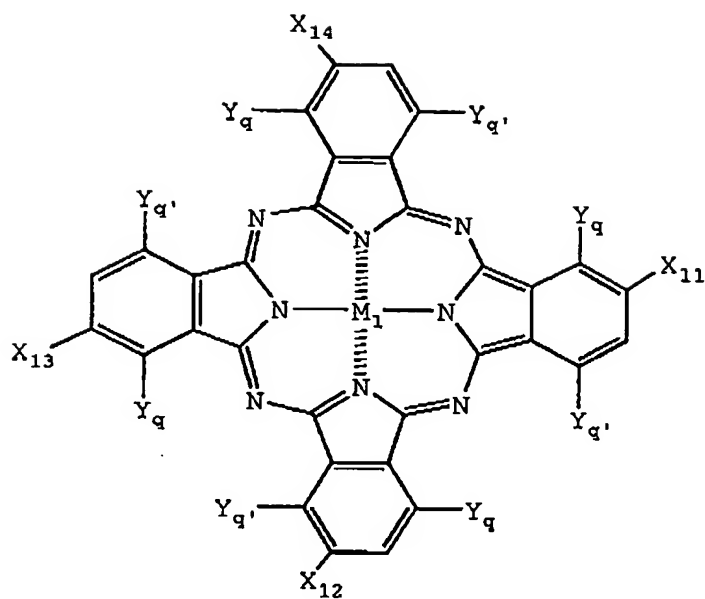
• Formula (a)-1:



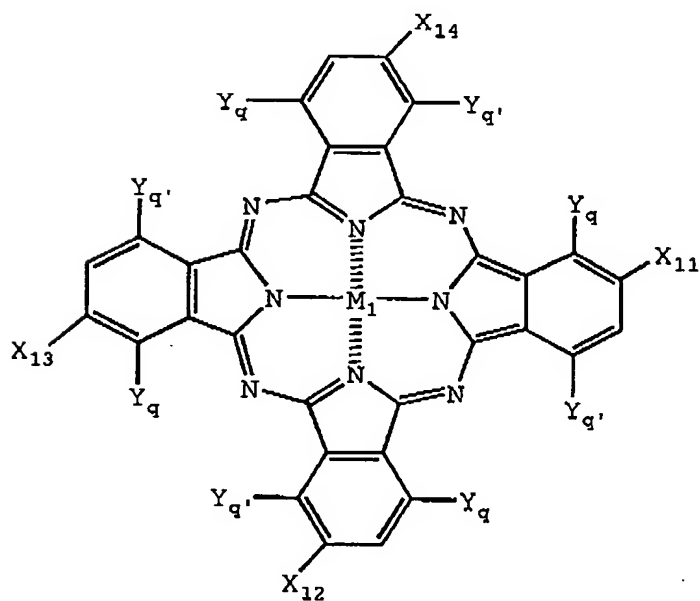
Formula (a)-2:



Formula (a)-3:



Formula (a)-4:



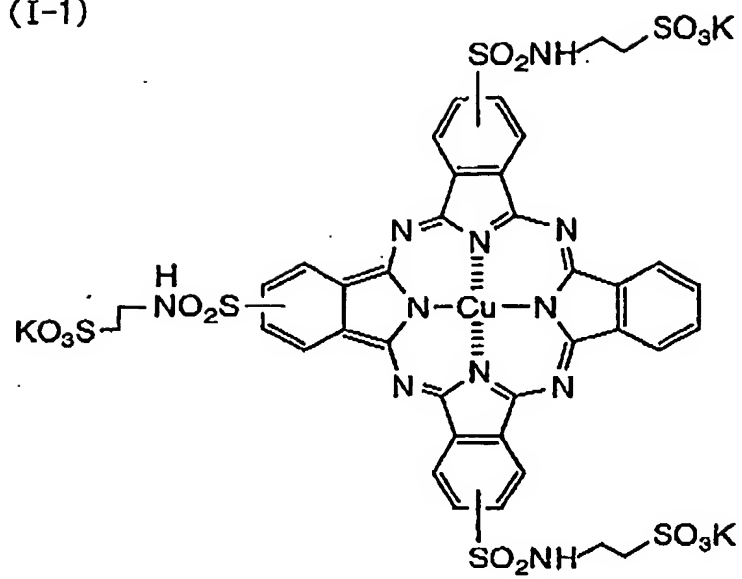
In the synthesis method above, when all  $X_p$ s are the

same; a  $\beta$ -position substitution type phthalocyanine dye where  $X_{11}$ ,  $X_{12}$ ,  $X_{13}$  and  $X_{14}$  are completely the same substituents can be obtained. On the other hand, when  $X_p$ s are different, a dye having substituents of the same kind but partially different from each other or a dye having substituents different from each other can be synthesized. Among the dyes of formula (CII), the dyes having electron-withdrawing substituents different from each other are preferred because the solubility and aggregation property of dye and the aging stability of ink can be controlled.

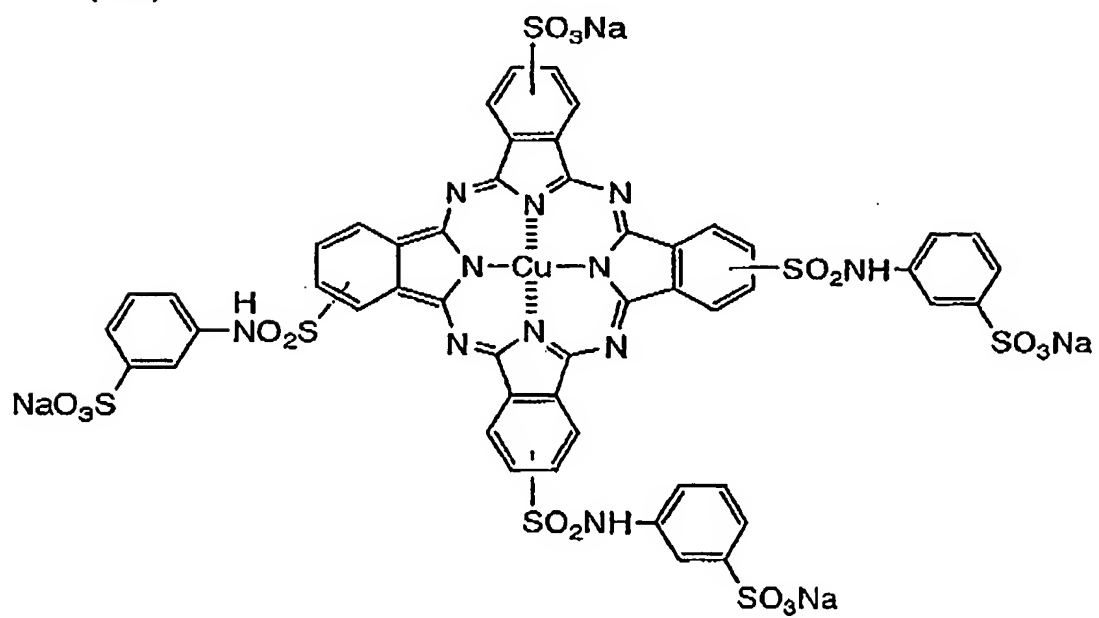
In the present invention, it has been found very important in any substitution type for the improvement of fastness that the oxidation potential is more positive than 1.0 V (vs SCE). The great effect thereof cannot be expected at all from the above-described related techniques. Furthermore, although the reason is not entirely known, there is a tendency that the  $\beta$ -position substitution type is apparently more excellent in the color hue, light fastness, ozone gas resistance and the like than the  $\alpha,\beta$ -position mixed substitution type.

Specific examples (Compounds I-1 to I-12 and 101 to 190) of the phthalocyanine dyes represented by formulae (CI) and (CII) are set forth below, however, the phthalocyanine dye for use in the present invention is not limited to the following examples.

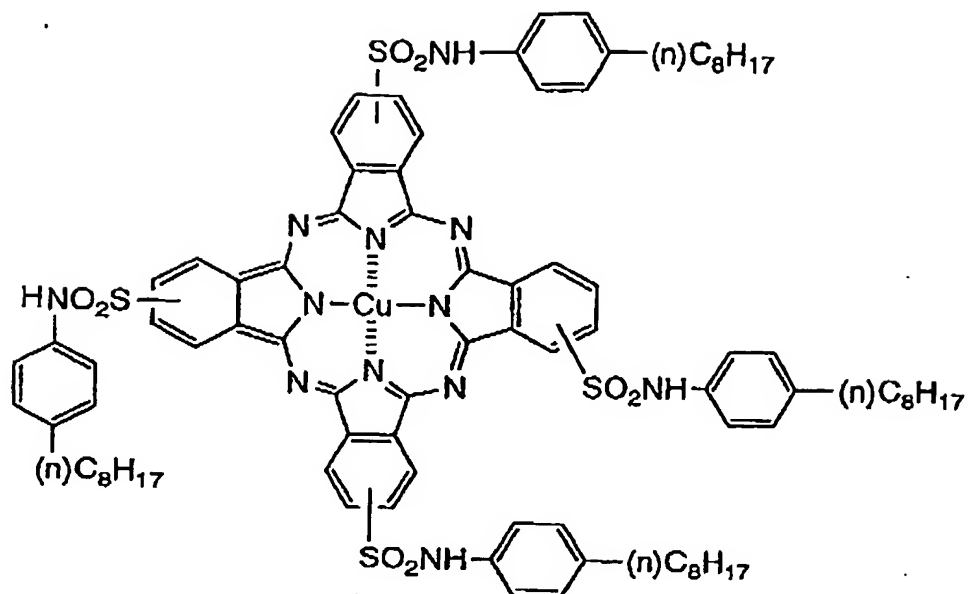
(I-1)



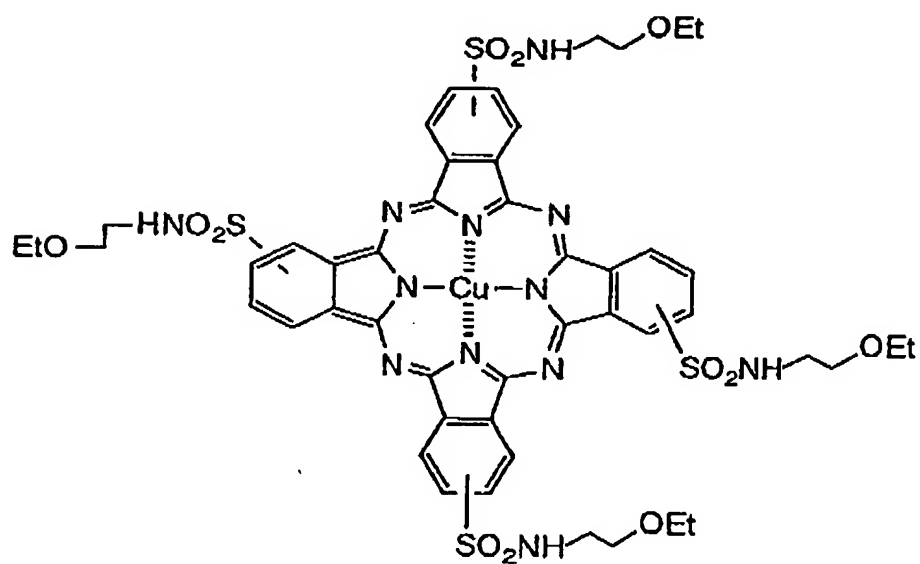
(I-2)



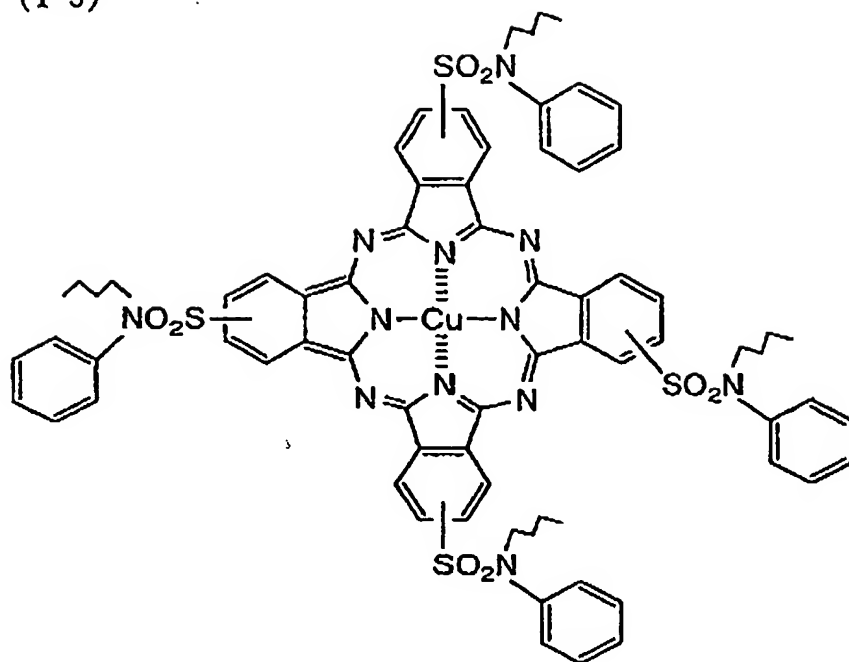
(I-3)



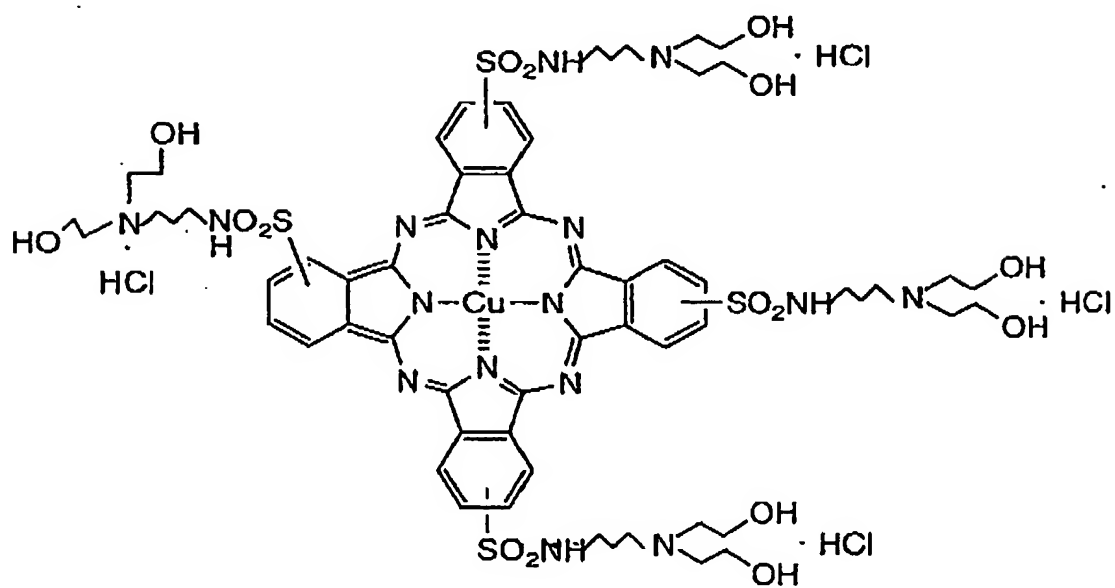
(I-4)



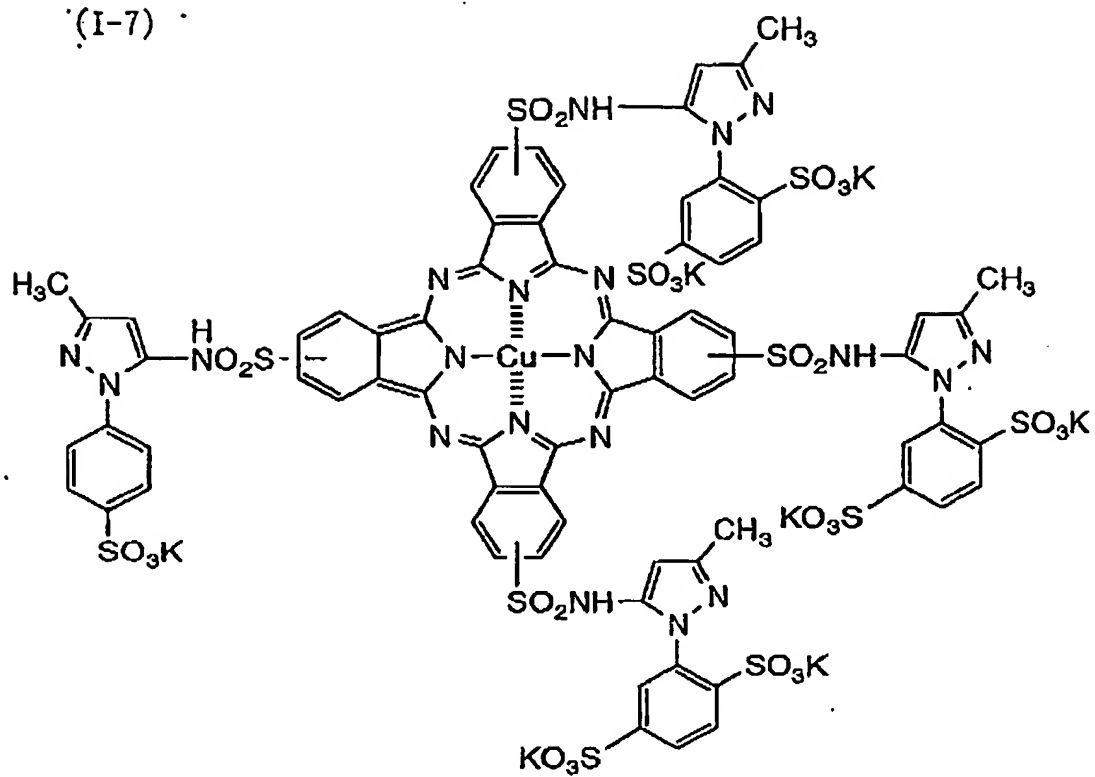
(I-5)



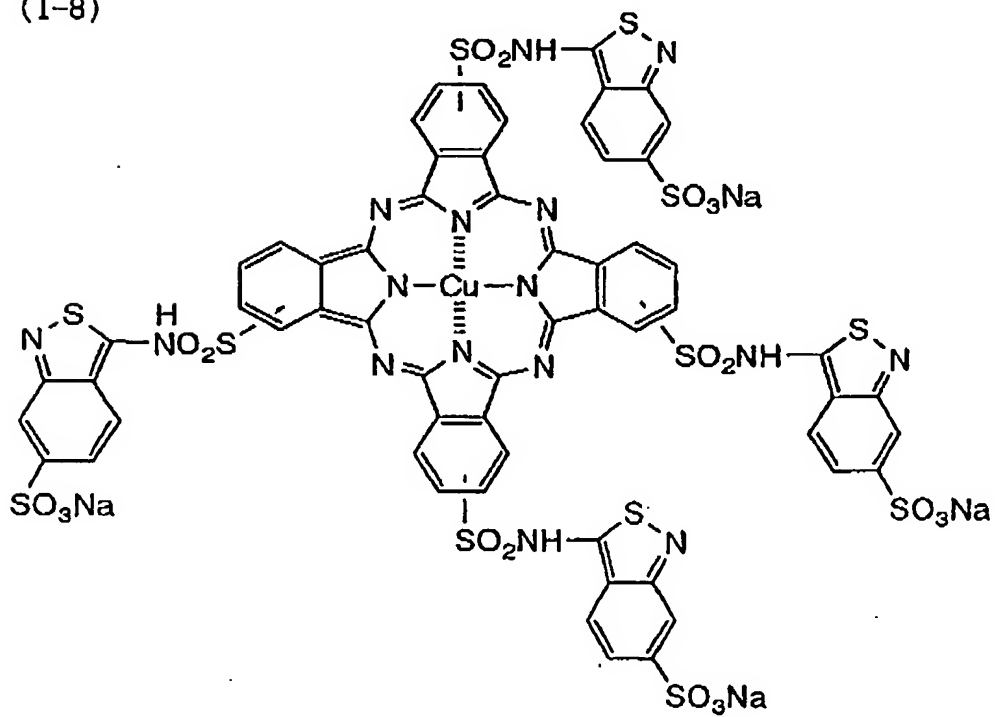
(I-6)



(I-7)

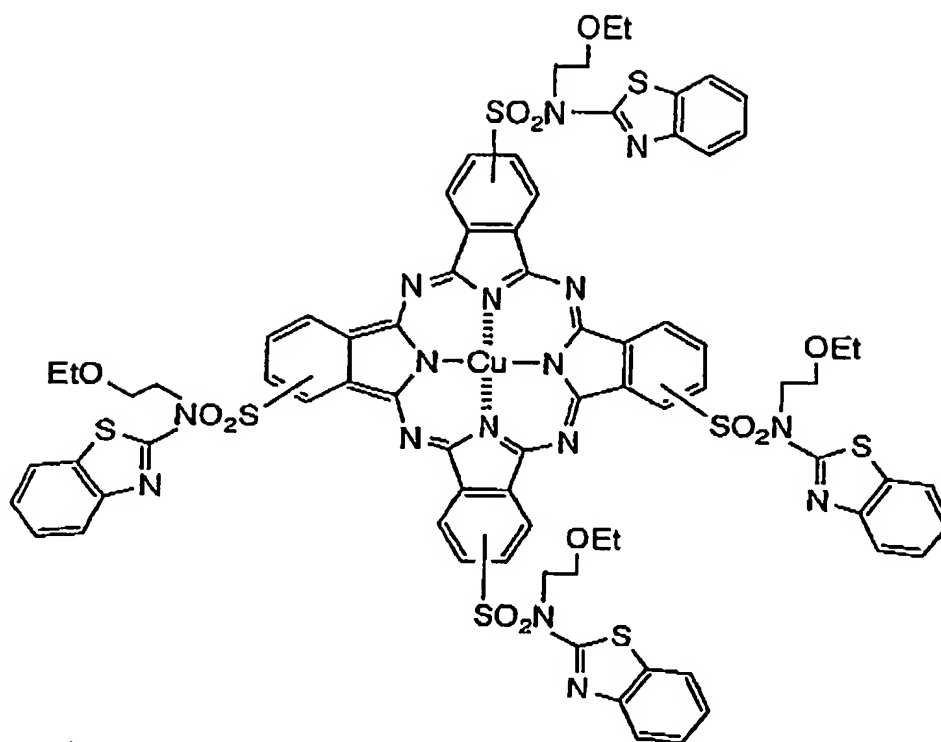


(I-8)

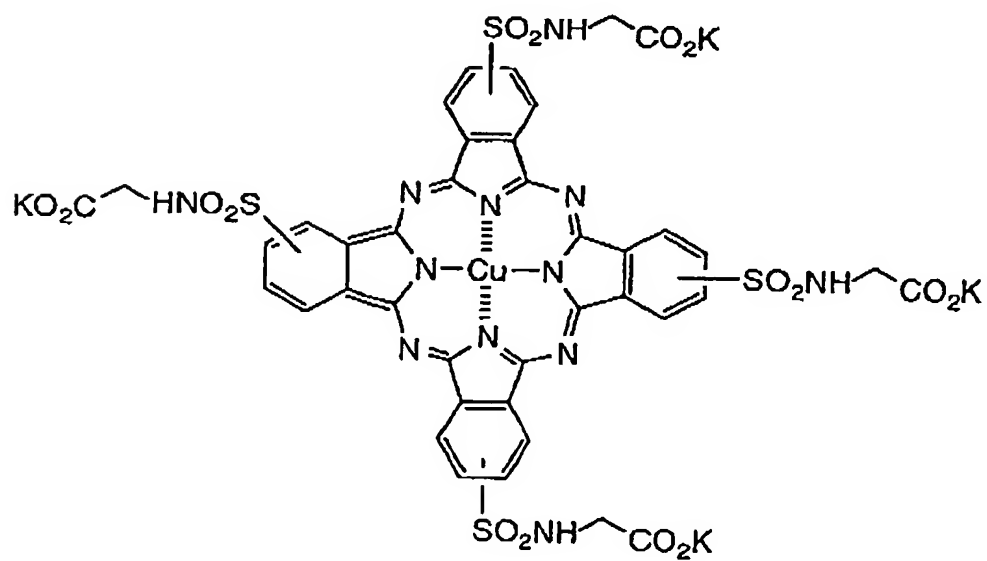




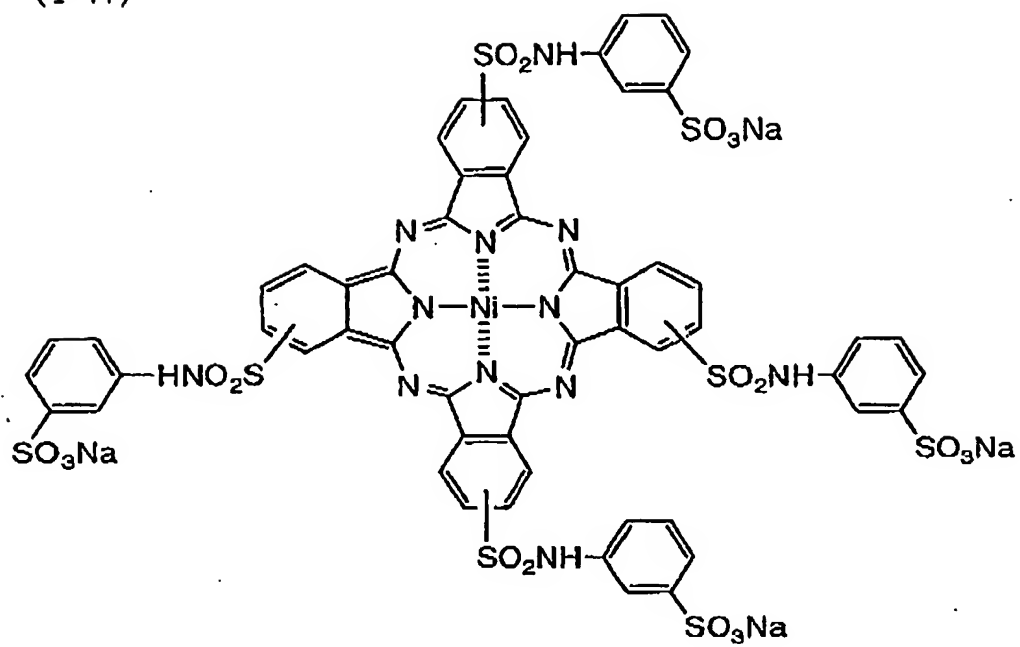
(I-9)



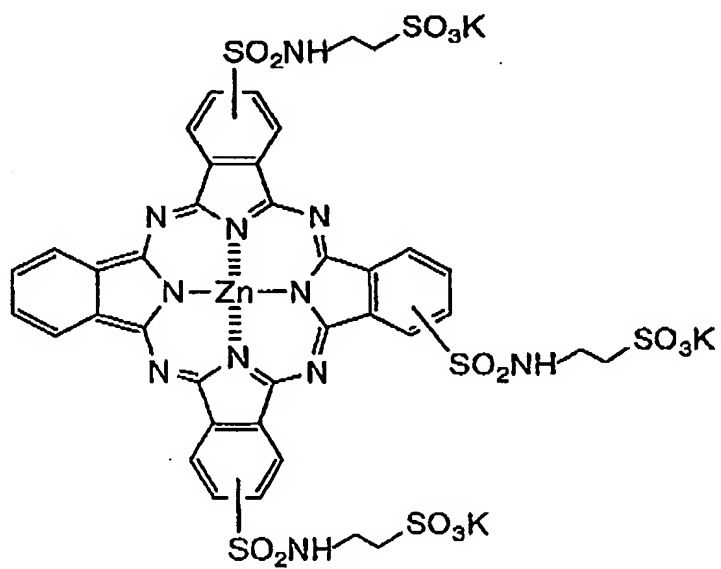
(I-10)

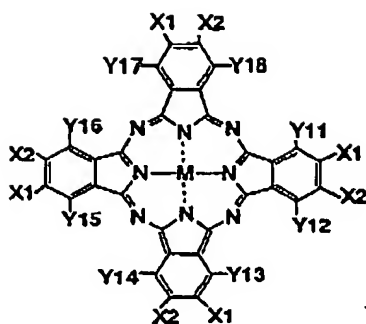


(I-11)



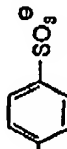
(I-12)





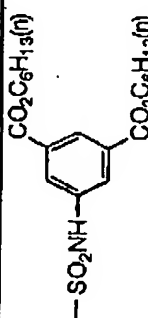
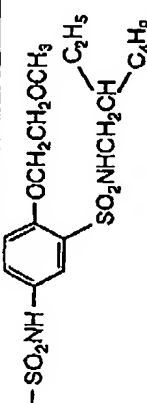
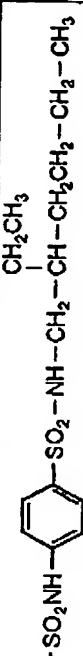
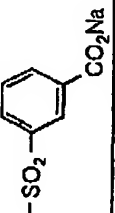
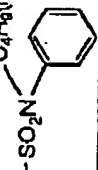
In the following tables, in the specific examples such as pairs (X1, X2), (Y11, Y12), (Y13, Y14), (Y15, Y16) and (Y17, Y18), the positions of each of members of the given pair are exchangeable with each other. For example, the position of X1 can be exchanged with the position of X2.

No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
101	Cu	$-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
102	Cu	$-\text{SO}_2-\text{NH}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2-\text{SO}_3\text{Na}$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
103	Cu	$-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_2\text{NH}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\text{CH}_2-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
104	Cu	$-\text{SO}_2-\text{NH}-\text{C}_6\text{H}_4-\text{SO}_2\text{NH}-\text{CH}_2\text{CH}_2-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
105	Ni	$-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CO}-\underset{\text{CH}_2-\text{COONa}}{\text{NH}}-\text{CH}-\text{COONa}$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
106	Cu	$-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\underset{\text{CH}_2-\text{COONa}}{\text{CH}}-\text{CH}_2-\text{COONa}$	-CN	-H, -H	-H, -H	-H, -H	-H, -H
107	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\underset{\text{CH}_2-\text{OH}}{\text{NH}}-\text{CH}-\text{COOLi}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
108	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
109	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{K}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
110	Cu	$-\text{SO}_2-(\text{CH}_2)_5-\text{CO}_3\text{K}$	-H	-H, -H	-H, -H	-H, -H	-H, -H

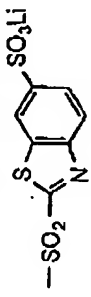
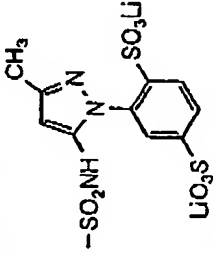
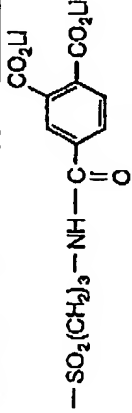
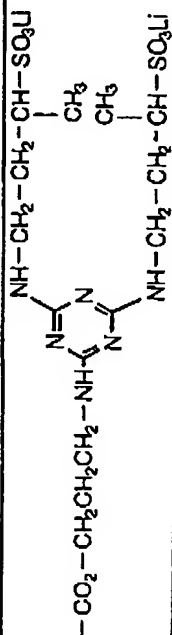
No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
111	Cu	$-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
112	Cu	$-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$	$-\text{SO}_3\text{Li}$	-H, -H	-H, -H	-H, -H	-H, -H
113	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{SO}_3\text{K}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
114	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$	$-\text{SO}_3\text{Li}$	-H, -H	-H, -H	-H, -H	-H, -H
115	Cu	$-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2 \cdot \text{CH}_3$ 	-H	-H, -H	-H, -H	-H, -H	-H, -H
116	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{SO}_3\text{K}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
117	Cu	$-\text{CO}-\text{NH}-\text{CH}(\text{COOLi})-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H

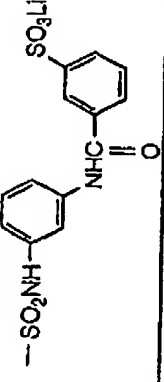
No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
118	Cu	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{SO}_2\text{CH}_2\text{CH}_2\text{CH} - \text{SO}_3\text{Li} \end{array}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
119	Cu	$\begin{array}{c} \text{OH} \\   \\ -\text{SO}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{SO}_3\text{Na} \end{array}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
120	Cu	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{COOLi} \end{array}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
121	Cu	$\begin{array}{c} \text{OH} \\   \\ -\text{SO}_2(\text{CH}_2)_3\text{SO}_2\text{NHCH}_2-\text{CH}-\text{CH}_2-\text{SO}_3\text{Li} \end{array}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
122	Cu	$\begin{array}{c} \text{OH} \\   \\ -\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{SO}_3\text{Li} \end{array}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
123	Cu	$-\text{SO}_2\text{NH}-\text{C}_6\text{H}_{11}(\text{t})$	-H	-H, -H	-H, -H	-H, -H	-H, -H
124	Cu	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ -\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}-\text{CH}_2\text{CHCH}_2-\text{CH}_3 \end{array}$	-H	-H, -H	-H, -H	-H, -H	-H, -H

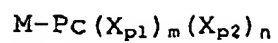
No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
125	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2-\text{NH}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
126	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{O}-\text{CH}_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
127	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{O}-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\overset{\text{CH}_3}{\text{CH}_3}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
128	Zn	$-\text{SO}_2-\text{CH}_2-\overset{\text{O}-\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{O}-\text{CH}_2$	-CN	-H, -H	-H, -H	-H, -H	-H, -H
129	Cu	$-\text{CO}-\text{NH}-\overset{\text{CH}_2\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{CH}_3$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
130	Cu	$-\text{CO}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{O}-\text{C}_4\text{H}_9(\text{I})$	-H	-H, -H	-H, -H	-H, -H	-H, -H
131	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{SO}_2-\text{NH}-\text{C}_6\text{H}_4-\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H

No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
132	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
133	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
134	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
135	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
136	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H



No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
137	Cu	 <chem>S=C1N=C(NC(=S)C1)S(=O)(=O)c2ccc(cc2)S(=O)(=O)[Li]</chem>	-H	-H, -H	-H, -H	-H, -H	-H, -H
138	Cu	 <chem>Cc1cc(C(=N1)NS(=O)(=O)c2ccc(cc2)S(=O)(=O)[Li])nn1</chem>	-H	-H, -H	-H, -H	-H, -H	-H, -H
139	Cu	 <chem>OS(=O)(=O)c1ccc(cc1NC(=O)c2ccc(cc2)C(=O)O[Li])C(=O)O[Li]</chem>	-Cl	-H, -H	-H, -H	-H, -H	-H, -H
140	Cu	 <chem>OS(=O)(=O)CCc1cc(C(=N1)NC2=NC(=NC(=N2)NC3CC(C)C3S(=O)(=O)O[Li])S(=O)(=O)O[Li])nn1</chem>	-H	-H, -H	-H, -H	-H, -H	-H, -H

No.	M	X1	X2	Y11, Y12	Y13, Y14	Y15, Y16	Y17, Y18
141	Cu	$\text{--SO}_2\text{NH--CH(CH}_2\text{COONa)--CH}_2\text{--CO--N--(CH}_2\text{CH}_2\text{OH)}_2$	-H	-H, -H	-H, -H	-H, -H	-H, -H
142	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
143	Cu	$\text{--CO--NH--CH}_2\text{--CH(OH)--CO--NH--CH(COOK)--CH}_2\text{CH}_2\text{--SO}_3\text{K}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
144	Cu	$\text{--SO}_2\text{--CH}_2\text{CH}_2\text{CH}_2\text{--NH--CO--C}_6\text{H}_4\text{--CO--NH--CH(COOLi)--CH}_2\text{--COOLi}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
145	Cu	$\text{--SO}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SO}_3\text{Li}$	-H	-H, -H	-H, -H	-H, -H	-H, -H



In the following tables, the introduction positions of the substituents  $(X_{p1})$  and  $(X_{p2})$  in each compound are exchangeable with each other in the  $\beta$ -position substitution type phthalocyanine dye.

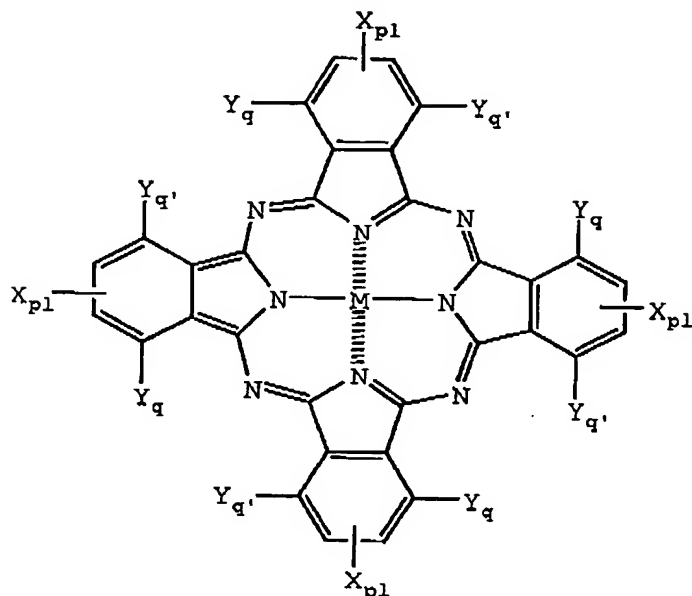


No.	M	Xp <sub>1</sub>	m	Xp <sub>1</sub>	n
158	Cu	$-\text{SO}_2-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{SO}_3\text{Li}$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{OH}$	1
159	Cu	$-\text{SO}_2\text{NHCH}_2\text{CH}_3-\text{SO}_3\text{Li}$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}-\text{CH}_3$	1
160	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\overset{\text{CH}_2-\text{CH}_2-\text{COONa}}{\underset{ }{\text{NH}}}-\text{CH}_2-\text{COONa}$	1
161	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Li}$	3	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2\text{SO}_3\text{Li}$	1
162	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Li}$	2	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	2
163	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{K}$	3	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NH}-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{OH}$	1
164	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Li}$	2	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$	2
165	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{K}$	3	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$	1
166	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{COONa}$	3	$-\text{CO}-\text{NH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	1
167	Cu	$-\text{SO}_2(\text{CH}_2)_3\text{SO}_2\text{NHCH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2\text{CO}_2\text{Li}$	2.5	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{N}-(\text{CH}_2-\text{CH}_2-\text{OH})_2$	1.5
168	Cu	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{SO}_3\text{Na}$	2	$-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{N}-(\text{CH}_2-\text{CH}_2-\text{OH})_2$	2
169	Cu	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Li}$	3	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	1
170	Cu	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOK}$	2	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{COOK}$	2



No.	M	$X_{D1}$	m	$X_{D2}$	n
183	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2-\text{NH}-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$	2	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-(\text{CH}_2)_2-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{OH}$	2
184	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2$	1
185	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2$	1
186	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2-\text{NH}-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{OH}$	1
187	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}-(\text{CH}_3)_2$	3	$-\text{CO}_2-\text{CH}_2-\overset{\text{CH}_2\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{CH}_3$	1
188	Cu	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2-\text{NH}-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$	3	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2$	1
189	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}-(\text{CH}_3)_2$	3	$-\text{SO}_2-\text{NH}-\text{CH}_2-\overset{\text{CH}_2\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	1
190	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\overset{\text{CH}_2\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{CH}_3$	3	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2$	1

The structure of the phthalocyanine compound represented by  $M\text{-Pc}(X_{p1})_m(X_{p2})_n$  regarding Compound Nos. 146 to 190 is shown below:



(wherein each  $X_{p1}$  represents independently  $X_{p1}$  or  $X_{p2}$  shown in the tables.)

The phthalocyanine dye represented by formula (CI) can be synthesized according to the patent publications described above. Furthermore, the phthalocyanine dye represented by formula (CII) can be synthesized by the methods described in JP-A-2001-226275, JP-A-2001-96610, JP-A-2001-47013 and JP-A-2001-193638 in addition to the above-described synthesis method. The starting material, dye intermediate and synthesis route are not limited to those



described in the patent publications.

The inkjet recording ink of the present invention contains the phthalocyanine dye in an amount of preferably from 0.2 to 20 wt%, more preferably from 0.5 to 15 wt%.

The inkjet recording cyan ink of the present invention can be prepared by dissolving and/or dispersing a cyan dye, preferably the phthalocyanine dye in an aqueous medium. The term "aqueous medium" as used in the present invention means water or a mixture of water and a small amount of water-miscible organic solvent, where additives such as wetting agent (preferably a surfactant as a dissolution aid or dispersion aid), stabilizer or antiseptic are added, if desired.

[Magenta Dye]

In the magenta ink used for the inkjet recording ink of the present invention, a magenta dye selected from azo dyes is dissolved or dispersed in an aqueous medium and the dye is fundamentally characterized in that the absorption maximum in the aqueous medium is present in the spectral region of 500 to 580 nm and the oxidation potential is more positive than 1.0 V (vs SCE).

The first preferred structural feature of the azo dye is that the dye has a chromophore represented by the formula: (heterocyclic ring A<sup>31</sup>)-N=N-(heterocyclic ring B<sup>31</sup>). In such a case, the heterocyclic rings A<sup>31</sup> and B<sup>31</sup> may have

the same structure. Specifically, the heterocyclic rings A<sup>31</sup> and B<sup>32</sup> each is a 5- or 6-membered heterocyclic ring selected from pyrazole, imidazole, triazole, oxazole, thiazole, selenazole, pyridone, pyrazine, pyrimidine and pyridine. These are specifically described, for example, in JP-A-2001-279145, JP-A-2002-309116 and JP-A-2003-12650.

The second preferred structural feature of the azo dye is that an aromatic nitrogen-containing 6-membered heterocyclic ring is bonded as the coupling component directly to at least one side of the azo group. Specific examples thereof are described in JP-A-2002-371214.

The third preferred structural feature is that the auxochrome has an aromatic or heterocyclic ring amino group structure, specifically, an anilino group or a heterylamino group.

The fourth preferred structural feature is that the dye has a steric structure. The dye is specifically described in JP-A-2002-371214.

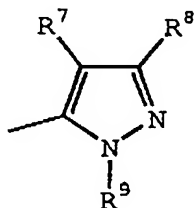
Among these preferred structural features of the azo dye, the dye most preferred for attaining the objects of the present invention is a dye represented by formula (MI) above.

The dye of formula (MI) is described in more detail below.

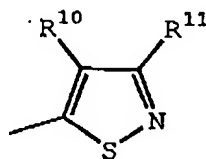
In formula (MI), A<sup>31</sup> represents a 5-membered hetero-

cyclic group. Examples of the heteroatom of the heterocyclic ring include N, O and S. A<sup>31</sup> is preferably a nitrogen-containing 5-membered heterocyclic ring and the heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or other heterocyclic ring. Preferred examples of the heterocyclic ring include a pyrazole ring, an imidazole ring, a thiazole ring, an isothiazole ring, a thiadiazole ring, a benzothiazole ring, a benzoxazole ring and a benzisothiazole ring. Each heterocyclic group may further have a substituent. Among those rings, more preferred are a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring and a benzothiazole ring represented by the following formulae (a) to (f):

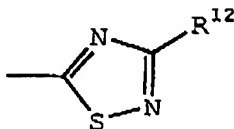
(a)



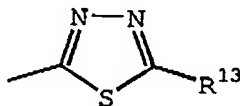
(b)



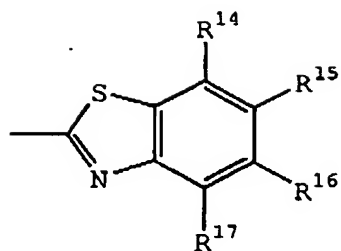
(c)



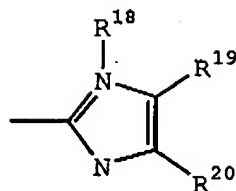
(d)



(e)



(f)



wherein R<sup>7</sup> to R<sup>20</sup> each represents a substituent same as the substituent for G<sup>31</sup>, R<sup>1</sup> or R<sup>2</sup> in formula (MI).

Among formulae (a) to (f), preferred are a pyrazole ring and an isothiazole ring represented by formulae (a) and (b), and most preferred is a pyrazole ring represented by formula (a).

In formula (MI), B<sup>31</sup> and B<sup>32</sup> each represents =CR<sup>1</sup>- or -CR<sup>2</sup>=, or either one of B<sup>31</sup> and B<sup>32</sup> represents a nitrogen atom and the other represents =CR<sup>1</sup>- or -CR<sup>2</sup>=. B<sup>31</sup> and B<sup>32</sup> each preferably represents =CR<sup>1</sup>- or -CR<sup>2</sup>=.

R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted.

R<sup>5</sup> and R<sup>6</sup> each is preferably a hydrogen atom, an

aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group, and the hydrogen atom of each substituent may be substituted, but  $R^5$  and  $R^6$  are not hydrogen atoms at the same time.

$G^{31}$ ,  $R^1$  and  $R^2$  each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy-carbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an

arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted.

G<sup>31</sup> is preferably a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, a heterocyclic oxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylthio group, an arylthio group or a heterocyclic thio group, more preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group (preferably an anilino group) or an acylamino group, and the hydrogen atom of each substituent may be substituted.

R<sup>1</sup> and R<sup>2</sup> each is preferably a hydrogen atom, an alkyl group, a halogen atom, an alkoxycarbonyl group, a carboxyl group, a carbamoyl group, a hydroxy group, an alkoxy group or a cyano group, and the hydrogen atom of each substituent may be substituted.

R<sup>1</sup> and R<sup>5</sup>, or R<sup>5</sup> and R<sup>6</sup> may combine to form a 5- or 6-

membered ring.

When  $A^{31}$  has a substituent or when the substituent  $R^1$ ,  $R^2$ ,  $R^5$ ,  $R^6$  or  $G^{31}$  further has a substituent, examples of the substituent include the substituents described above for  $G^{31}$ ,  $R^1$  and  $R^2$ .

In the case where the dye of formula (MI) of the present invention is a water-soluble dye, the dye preferably further contains an ionic hydrophilic group as a substituent on any position of  $A^{31}$ ,  $R^1$ ,  $R^2$ ,  $R^5$ ,  $R^6$  and  $G^{31}$ . Examples of the ionic hydrophilic group as a substituent include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among the ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include an ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium).

The term "substituents" as used in the present invention is described below. The term is common among different symbols in formula (MI) and also in formula (MIa) shown later.

The halogen atom includes a fluorine atom, a chlorine atom and a bromine atom.

The aliphatic group means an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an aralkyl group and a substituted aralkyl group. A "substituted" used for the "substituted alkyl group" and the like in the present invention means that the hydrogen atom present in an "alkyl group" or the like is substituted, for example, by the substituent described above for  $G^{31}$ ,  $R^1$  or  $R^2$ .

The aliphatic group may be branched or may form a ring. The number of carbon atoms in the aliphatic group is preferably from 1 to 20, more preferably from 1 to 16. The aryl moiety in the aralkyl group and the substituted aralkyl group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. Examples of the aliphatic group include a methyl group, an ethyl group, a butyl group, an isopropyl group, a tert-butyl group, a hydroxyethyl group, a methoxyethyl group, a cyanoethyl group, a trifluoromethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a cyclohexyl group, a benzyl group, a 2-phenethyl group, a vinyl group and an allyl group.

The aromatic group means an aryl group and a substituted aryl group. The aryl group is preferably a



phenyl group or a naphthyl group, more preferably a phenyl group. The number of carbon atoms in the aromatic group is preferably from 6 to 20, more preferably from 6 to 16.

Examples of the aromatic group include a phenyl group, a p-tolyl group, a p-methoxyphenyl group, an o-chlorophenyl group and an m-(3-sulfopropylamino)phenyl group.

The heterocyclic group includes a substituted heterocyclic group. In the heterocyclic group, the heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or other heterocyclic ring. The heterocyclic group is preferably a 5- or 6-membered heterocyclic group. Examples of the substituent of the substituted heterocyclic group include an aliphatic group, a halogen atom, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfamoyl group, a carbamoyl group and an ionic hydrophilic group. Examples of the heterocyclic group include a 2-pyridyl group, a 2-thienyl group, a 2-thiazolyl group, a 2-benzothiazolyl group, a 2-benzoxazolyl group and a 2-furyl group.

The carbamoyl group includes a substituted carbamoyl group. Examples of the substituent include an alkyl group. Examples of the carbamoyl group include a methylcarbamoyl group and a dimethylcarbamoyl group.

The alkoxycarbonyl group includes a substituted alkoxycarbonyl group. The alkoxycarbonyl group is

preferably an alkoxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonyl group include a methoxycarbonyl group and an ethoxycarbonyl group.

The aryloxy carbonyl group includes a substituted aryloxy carbonyl group. The aryloxy carbonyl group is preferably an aryloxy carbonyl group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aryloxy carbonyl group include a phenoxycarbonyl group.

The heterocyclic oxycarbonyl group includes a substituted heterocyclic oxycarbonyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic oxycarbonyl group is preferably a heterocyclic oxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic oxycarbonyl group include a 2-pyridyloxycarbonyl group.

The acyl group includes a substituted acyl group. The acyl group is preferably an acyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyl group include an acetyl group and a benzoyl group.

The alkoxy group includes a substituted alkoxy group.

The alkoxy group is preferably an alkoxy group having from 1 to 20 carbon atoms. Examples of the substituent include an alkoxy group, a hydroxyl group and an ionic hydrophilic group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an isopropoxy group, a methoxyethoxy group, a hydroxyethoxy group and a 3-carboxypropoxy group.

The aryloxy group includes a substituted aryloxy group. The aryloxy group is preferably an aryloxy group having from 6 to 20 carbon atoms. Examples of the substituent include an alkoxy group and an ionic hydrophilic group. Examples of the aryloxy group include a phenoxy group, a p-methoxyphenoxy group and an o-methoxyphenoxy group.

The heterocyclic oxy group includes a substituted heterocyclic oxy group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic oxy group is preferably a heterocyclic oxy group having from 2 to 20 carbon atoms. Examples of the substituent include an alkyl group, an alkoxy group and an ionic hydrophilic group. Examples of the heterocyclic oxy group include a 3-pyridyloxy group and a 3-thienyloxy group.

The silyloxy group is preferably a silyloxy group substituted by an aliphatic or aromatic group having from 1

to 20 carbon atoms. Examples of the silyloxy group include a trimethylsilyloxy group and a diphenylmethylsilyloxy group.

The acyloxy group includes a substituted acyloxy group. The acyloxy group is preferably an acyloxy group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyloxy group include an acetoxy group and a benzoyloxy group.

The carbamoyloxy group includes a substituted carbamoyloxy group. Examples of the substituent include an alkyl group. Examples of the carbamoyloxy group include an N-methylcarbamoyloxy group.

The alkoxycarbonyloxy group includes a substituted alkoxycarbonyloxy group. The alkoxycarbonyloxy group is preferably an alkoxycarbonyloxy group having from 2 to 20 carbon atoms. Examples of the alkoxycarbonyloxy group include a methoxycarbonyloxy group and an isopropoxycarbonyloxy group.

The aryloxcarbonyloxy group includes a substituted aryloxcarbonyloxy group. The aryloxcarbonyloxy group is preferably an aryloxcarbonyloxy group having from 7 to 20 carbon atoms. Examples of the aryloxcarbonyloxy group include a phenoxycarbonyloxy group.

The amino group includes a substituted amino group.

Examples of the substituent include an alkyl group, an aryl group and a heterocyclic group, and the alkyl group, the aryl group and the heterocyclic group each may further have a substituent. The alkylamino group includes a substituted alkylamino group. The alkylamino group is preferably an alkylamino group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylamino group include a methylamino group and a diethylamino group.

The arylamino group includes a substituted arylamino group. The arylamino group is preferably an arylamino group having from 6 to 20 carbon atoms. Examples of the substituent include a halogen atom and an ionic hydrophilic group. Examples of the arylamino group include a phenylamino group and a 2-chlorophenylamino group.

The heterocyclic amino group includes a substituted heterocyclic amino group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic amino group is preferably a heterocyclic amino group having from 2 to 20 carbon atoms. Examples of the substituent include an alkyl group, a halogen atom and an ionic hydrophilic group.

The acylamino group includes a substituted acylamino group. The acylamino group is preferably an acylamino group having from 2 to 20 carbon atoms. Examples of the

substituent include an ionic hydrophilic group. Examples of the acylamino group include an acetylamino group, a propionylamino group, a benzoylamino group, an N-phenylacetylamino group and a 3,5-disulfobenzoylamino group.

The ureido group includes a substituted ureido group. The ureido group is preferably a ureido group having from 1 to 20 carbon atoms. Examples of the substituent include an alkyl group and an aryl group. Examples of the ureido group include a 3-methylureido group, a 3,3-dimethylureido group and a 3-phenylureido group.

The sulfamoylamino group includes a substituted sulfamoylamino group. Examples of the substituent include an alkyl group. Examples of the sulfamoylamino group include an N,N-dipropylsulfamoylamino group.

The alkoxycarbonylamino group includes a substituted alkoxycarbonylamino group. The alkoxycarbonylamino group is preferably an alkoxycarbonylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonylamino group include an ethoxycarbonylamino group.

The aryloxycarbonylamino group includes a substituted aryloxycarbonylamino group. The aryloxycarbonylamino group is preferably an aryloxycarbonylamino group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aryloxycarbonyl-

amino group include a phenoxy-carbonylamino group.

The alkylsulfonylamino group and the arylsulfonylamino group include a substituted alkylsulfonylamino group and a substituted arylsulfonylamino group, respectively. The alkylsulfonylamino group and the arylsulfonylamino group are preferably an alkylsulfonylamino group having from 1 to 20 carbon atoms and an arylsulfonylamino group having from 7 to 20 carbon atoms, respectively. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylsulfonylamino group and arylsulfonylamino group include a methylsulfonylamino group, an N-phenyl-methylsulfonylamino group, a phenylsulfonylamino group and a 3-carboxyphenylsulfonylamino group.

The heterocyclic sulfonylamino group includes a substituted heterocyclic sulfonylamino group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfonylamino group is preferably a heterocyclic sulfonylamino group having from 1 to 12 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfonylamino group include a 2-thienylsulfonylamino group and a 3-pyridylsulfonylamino group.

The alkylthio group, the arylthio group and the heterocyclic thio group include a substituted alkylthio

group, a substituted arylthio group and a substituted heterocyclic thio group, respectively. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The alkylthio group, the arylthio group and the heterocyclic thio group are preferably those having from 1 to 20 carbon atoms, respectively. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylthio group, arylthio group and heterocyclic thio group include a methylthio group, a phenylthio group and a 2-pyridylthio group.

The alkylsulfonyl group and the arylsulfonyl group include a substituted alkylsulfonyl group and a substituted arylsulfonyl group, respectively. Examples of the alkylsulfonyl group and arylsulfonyl group include a methylsulfonyl group and a phenylsulfonyl group.

The heterocyclic sulfonyl group includes a substituted heterocyclic sulfonyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfonyl group is preferably a heterocyclic sulfonyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfonyl group include a 2-thienylsulfonyl group and a 3-pyridylsulfonyl group.



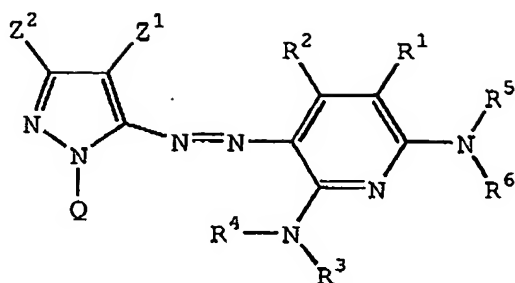
The alkylsulfinyl group and the arylsulfinyl group include a substituted alkylsulfinyl group and a substituted arylsulfinyl group, respectively. Examples of the alkylsulfinyl group and arylsulfinyl group include a methylsulfinyl group and a phenylsulfinyl group.

The heterocyclic sulfinyl group includes a substituted heterocyclic sulfinyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfinyl group is preferably a heterocyclic sulfinyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfinyl group include a 4-pyridylsulfinyl group.

The sulfamoyl group includes a substituted sulfamoyl group. Examples of the substituent include an alkyl group. Examples of the sulfamoyl group include a dimethylsulfamoyl group and a di-(2-hydroxyethyl)sulfamoyl group.

In the present invention, particularly preferred is a dye represented by the following formula (MIa):

Formula (MIa):



In formula (MIa),  $R^1$ ,  $R^2$ ,  $R^5$  and  $R^6$  have the same meanings as defined in formula (MI), respectively.

$R^3$  and  $R^4$  each independently represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group.  $R^3$  and  $R^4$  each is preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group or a heterocyclic group.

$Z^1$  represents an electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.20 or more.  $Z^1$  is preferably an electron-withdrawing group having a  $\sigma_p$  value of 0.30 or more, more preferably 0.45 or more, still more preferably 0.60 to more, but the  $\sigma_p$  value preferably does not exceed 1.0. Specific preferred examples of the

substituent include electron-withdrawing substituents described later. Among those, preferred are an acyl group having from 2 to 20 carbon atoms, an alkyloxycarbonyl group having from 2 to 20 carbon atoms, a nitro group, a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, an arylsulfonyl group having from 6 to 20 carbon atoms, a carbamoyl group having from 1 to 20 carbon atoms and a halogenated alkyl group having from 1 to 20 carbon atoms, more preferred are a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms and an arylsulfonyl group having from 6 to 20 carbon atoms, and most preferred is a cyano group.

$Z^2$  represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group or a heterocyclic group.  $Z^2$  is preferably an aliphatic group, more preferably an alkyl group having from 1 to 6 carbon atoms.

Q represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group or a heterocyclic group. Q is preferably a group comprising a nonmetallic atom group necessary for forming a 5-, 6-, 7- or 8-membered ring. The 5-, 6-, 7- or 8-membered ring may be substituted, may be a saturated ring or may have an unsaturated bond. Q is more preferably an aromatic group or a heterocyclic group. Preferred examples of the

nonmetallic atom include a nitrogen atom, an oxygen atom, a sulfur atom and a carbon atom. Specific examples of the ring structure include a benzene ring, a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, a cyclooctane ring, a cyclohexene ring, a pyridine ring, a pyrimidine ring, a pyrazine ring, a pyridazine ring, a triazine ring, an imidazole ring, a benzimidazole ring, an oxazole ring, a benzoxazole ring, a thiazole ring, a benzothiazole ring, an oxane ring, a sulfolane ring and a thiane ring.

The hydrogen atom of each substituent described in regard to formula (MIa) may be substituted. Examples of the substituent include the substituents described in regard to formula (MI), the groups described as examples for  $G^{31}$ ,  $R^1$  and  $R^2$ , and an ionic hydrophilic group.

The Hammett's substituent constant  $\sigma_p$  value used in the present invention is described. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a  $\sigma_p$  value and a  $\sigma_m$  value and these values can be found in a large number of conventional publications and they are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979),

and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979). In the present invention, each substituent is limited or described by using the Hammett's substituent constant  $\sigma_p$  but it does not mean that the substituent is limited only to those having a known value which can be found in the above-described publications. Needless to say, the substituent includes substituents of which  $\sigma_p$  value is not known in publications but when measured based on the Hammett's rule, falls within the range specified. Furthermore, although formula (1a) of the present invention include those which are not a benzene derivative, the  $\sigma_p$  value is used as a measure for showing the electron effect of the substituent irrespective of the substitution site. In the present invention, the  $\sigma_p$  value is used in such a meaning.

Examples of the electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.60 or more include a cyano group, a nitro group, an alkylsulfonyl group (e.g., methylsulfonyl) and an arylsulfonyl group (e.g., phenylsulfonyl).

Examples of the electron-withdrawing group having a Hammett's  $\sigma_p$  value of 0.45 or more include, in addition to those described above, an acyl group (e.g., acetyl), an alkoxycarbonyl group (e.g., dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., m-chlorophenoxycarbonyl), an

alkylsulfinyl group (e.g., n-propylsulfinyl), an arylsulfinyl group (e.g., phenylsulfinyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl) and a halogenated alkyl group (e.g., trifluoromethyl).

Examples of the electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.30 or more include, in addition to those described above, an acyloxy group (e.g., acetoxy), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a halogenated alkoxy group (e.g., trifluoromethyloxy), a halogenated aryloxy group (e.g., pentafluorophenyloxy), a sulfonyloxy group (e.g., methylsulfonyloxy), a halogenated alkylthio group (e.g., difluoromethylthio), an aryl group substituted by two or more electron-withdrawing groups having a  $\sigma_p$  value of 0.15 or more (e.g., 2,4-dinitrophenyl, pentachlorophenyl) and a heterocyclic ring (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl).

Specific examples of the electron-withdrawing group having a  $\sigma_p$  value of 0.20 or more include, in addition to those described above, a halogen atom.

The preferred combination of substituents in the azo dye represented by formula (MI) is described below.  $R^5$  and  $R^6$  each is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a sulfonyl group or an acyl group, more preferably a hydrogen atom, an aryl group,

a heterocyclic group or a sulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group. However,  $R^5$  and  $R^6$  are not hydrogen atoms at the same time.

$G^{31}$  is preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an amino group or an acylamino group, more preferably a hydrogen atom, a halogen atom, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group or an acylamino group.

$A^{31}$  is preferably a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring or a benzothiazole ring, more preferably a pyrazole ring or an isothiazole ring, and most preferably a pyrazole ring.

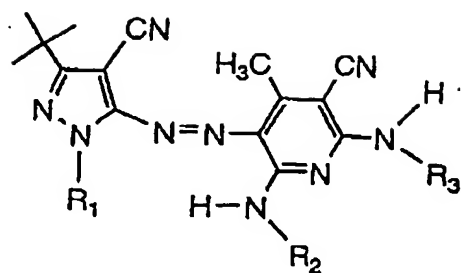
$B^{31}$  and  $B^{32}$  each is  $=CR^1-$  or  $-CR^2=$ , and  $R^1$  and  $R^2$  each is preferably a hydrogen atom, an alkyl group, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, a hydroxyl group, an alkoxy group or an alkoxycarbonyl group, more preferably a hydrogen atom, an alkyl group, a carboxyl group, a cyano group or a carbamoyl group.

As for the preferred combination of substituents in the compound represented by formula (MI), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred,

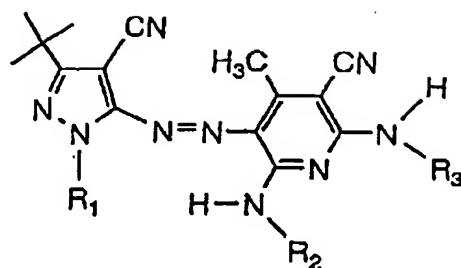
and a compound where all substituents are the preferred groups is most preferred. The dye represented by formula (MI) preferably contains an anionic group and as for the number of anionic groups, the dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, per molecule.

Specific examples of the compound (azo dye) represented by formula (MI) are set forth below, however, the azo dye for use in the present invention is not limited to those set forth below.

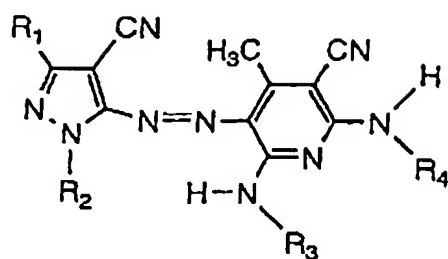




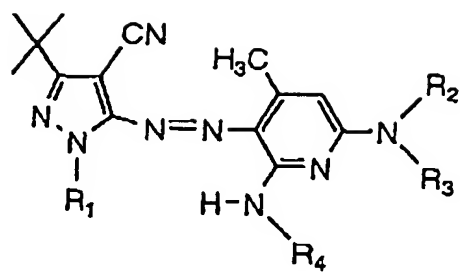
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
a-1			
a-2			
a-3			
a-4			
a-5			



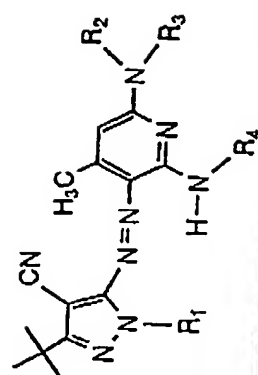
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
a-6			
a-7			
a-8			
a-9			
a-10			



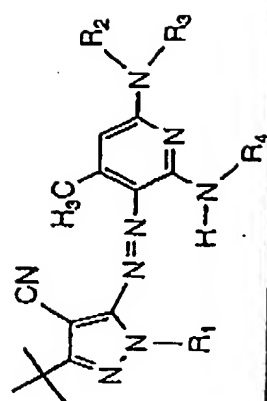
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-11				
a-12				
a-13				
a-14				
a-15				
a-16				
a-17				



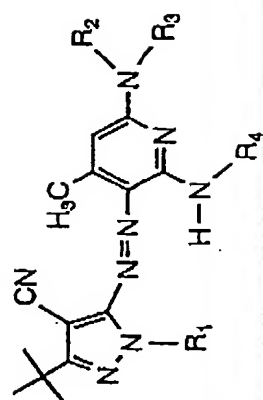
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-18				
a-19		-SO <sub>2</sub> CH <sub>3</sub>		
a-20		-COCH <sub>3</sub>	C <sub>8</sub> H <sub>17</sub> (t)	C <sub>8</sub> H <sub>17</sub> (t)
a-21		-SO <sub>2</sub> CH <sub>3</sub>		C <sub>8</sub> H <sub>17</sub> (t)
a-22		H		
a-23		H		
a-24		H		
a-25				



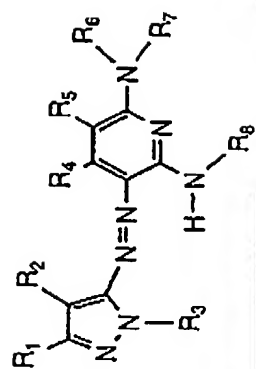
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-26				
a-27				
a-28				
a-29				
a-30				
a-31				



Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-32				
a-33				
a-34				
a-35				

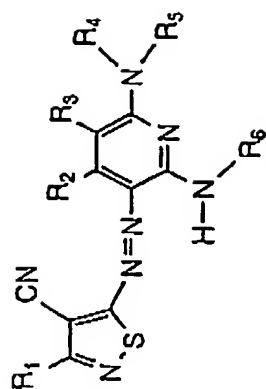


Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-36				
a-37				
a-38				
a-39				
a-40				

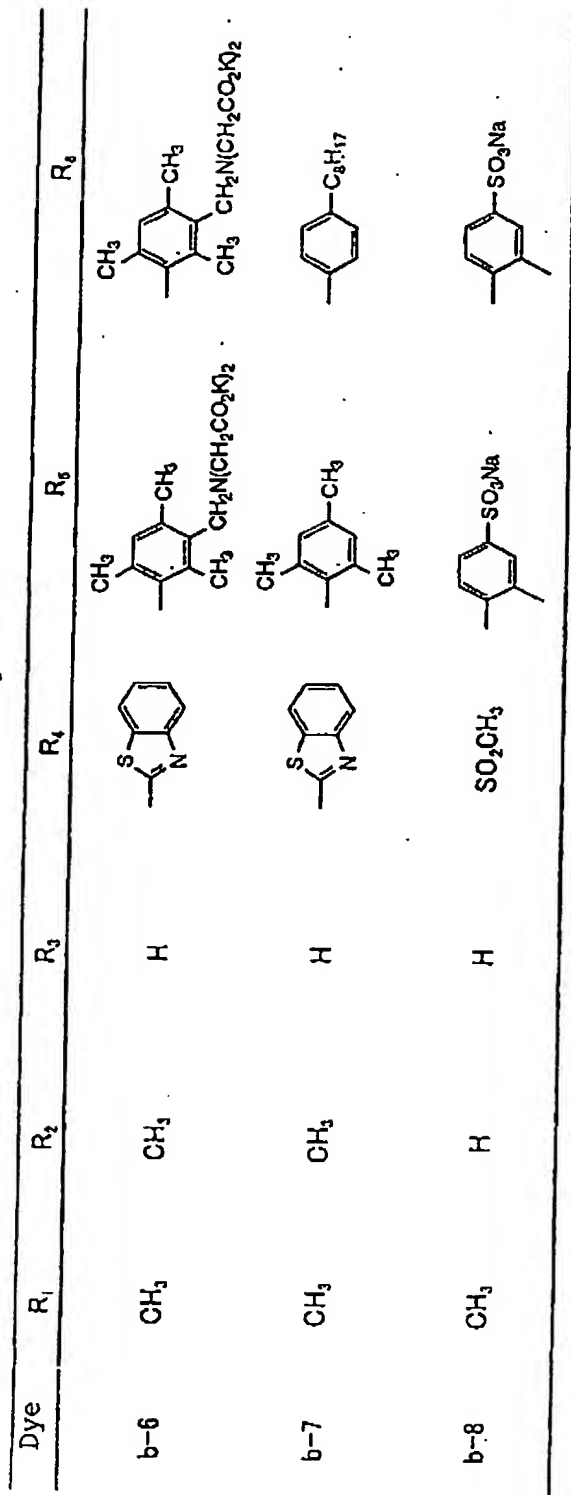


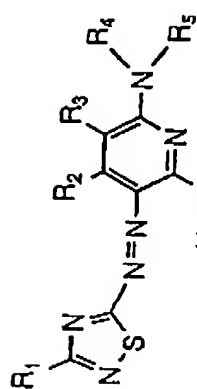
Dye	$R_1$	$R_2$	$R_3$	$R_4$	$R_5$	$R_6$	$R_7$	$R_8$
a-41		CN		H	CONH <sub>2</sub>	SO <sub>2</sub> CH <sub>3</sub>		
a-42		Br		COOEt	H		C <sub>8</sub> H <sub>17</sub> (t)	COCH <sub>3</sub>
a-43		SO <sub>2</sub> CH <sub>3</sub>		CONH <sub>2</sub>	H			
a-44		CN		H	H			SO <sub>2</sub> CH <sub>3</sub>
a-45		Br		H	CONH <sub>2</sub>			
a-46		CN		CH <sub>3</sub>	H			



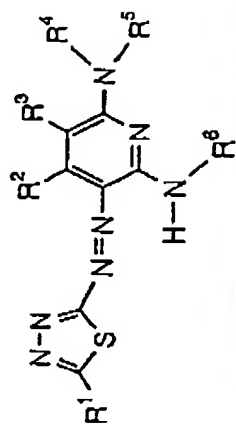


Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
b-1	CH <sub>3</sub>	CH <sub>3</sub>	CN	H		
b-2	CH <sub>3</sub>	CH <sub>3</sub>	CN	H		
b-3	CH <sub>3</sub>	CH <sub>3</sub>	CONH <sub>2</sub>	H		
b-4	CH <sub>3</sub>	CH <sub>3</sub>	H	H		
b-5	CH <sub>3</sub>	H	CN	H		

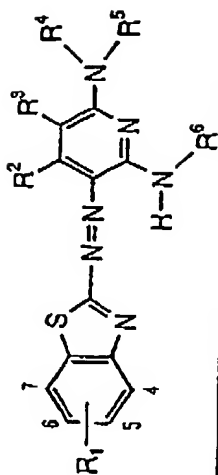




Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
c-1	-SCH <sub>3</sub>	CH <sub>3</sub>	CN	H	C <sub>8</sub> H <sub>17</sub> (t)	
c-2		H	CONH <sub>2</sub>	H		
c-3	-S-CH <sub>2</sub> -SO <sub>3</sub> K	CH <sub>3</sub>	H			
c-4	-CH <sub>3</sub>	CH <sub>3</sub>	H			
c-5		H	H			C <sub>8</sub> H <sub>17</sub> (t)

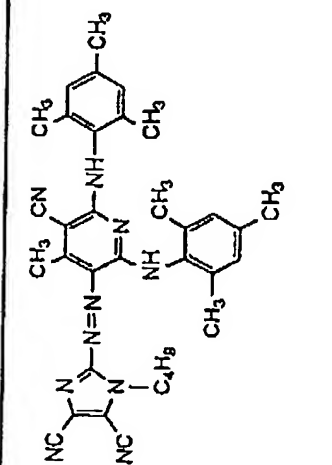


Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
d-1	Me	CH <sub>3</sub>	CN	H		
d-2	Me	CH <sub>3</sub>	CN	H		
d-3	Me	H	H			
d-4	Ph	CH <sub>3</sub>	CONH <sub>2</sub>	H		
d-5	Ph	CH <sub>3</sub>	H			



Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
e-1	5-Cl	CH <sub>3</sub>	CONH <sub>2</sub>	H	C <sub>8</sub> H <sub>17</sub> (t)	C <sub>8</sub> H <sub>17</sub> (t)
e-2	5,6-diCl	H	H			
e-3	5,6-diCl	CH <sub>3</sub>	H			COCH <sub>3</sub>
e-4	5-CH <sub>3</sub>	H	CN	H		
e-5	5-NO <sub>2</sub>	CH <sub>3</sub>	H	SO <sub>2</sub> CH <sub>3</sub>		

f-2



The magenta ink composition (hereinafter, sometimes simply referred to as "magenta ink") for inkjet recording of the present invention can be prepared by dissolving and/or dispersing a magenta dye, preferably at least one of the above-described azo dyes in an aqueous medium and preferably contains the azo dye in an amount of 0.2 to 20 wt%, more preferably from 0.5 to 15 wt%.

The azo dye for use in the present invention is substantially water-soluble. The term "substantially water-soluble" as used herein means that the dye dissolves in an amount of 2 wt% or more in water at 20°C.

In the inkjet ink composition of the present invention, other magenta dyes can be used in combination with the above-described azo dye (magenta dye).

Examples of the magenta dye which can be used in combination include aryl- or heteryl-azo dyes (except for the dye represented by formula (MI) of the present invention) having a phenol, a naphthol or an aniline as the coupling component; azomethine dyes having a pyrazolone or a pyrazolotriazole as the coupling component; methine dyes such as arylidene dye, styryl dye, merocyanine dye and oxonol dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; quinone-base dyes such as naphthoquinone, anthraquinone and anthrapyridone; and condensed polycyclic dyes such as dioxazine dye. These

dyes may be those which provide a magenta color for the first time when a part of the chromophore is dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure. In the ink composition containing the compound represented by formula (MI) of the present invention, other dye is used in combination within the range wherein the ink composition satisfies the ink precipitation test according to the present invention.

[Yellow Dye]

The yellow dye useful for the present invention is described in detail below.

A reflection density after printing an ink on a reflective medium is measured through a Status A filter (for example, X-rite 310TR Densitometer) and one point having a reflection density ( $D_B$ ) of 0.90 to 1.10 in the yellow region is defined as the initial density of the ink. Then, the printed matter is enforcedly discolored by using an ozone discoloration tester capable of always generating 5 ppm of ozone and the accelerated fading rate constant ( $k$ ) is determined according to  $(0.8=e^{-kt})$  from the time period ( $t$ ) until the reflection density decreases to 80% of the initial density, the yellow dye used in one ink

(composition) for use in the inkjet recording method of the present invention is controlled to have the accelerated fading rate constant of  $5.0 \times 10^{-2}$  [hour<sup>-1</sup>] or less, preferably  $3.0 \times 10^{-2}$  [hour<sup>-1</sup>] or less, more preferably  $1.0 \times 10^{-2}$  [hour<sup>-1</sup>] or less, in view of fastness and ozone gas resistance.

Also, the yellow dye is preferably a dye having an oxidation potential more positive than 1.0 V (vs SCE), more preferably more positive than 1.1 V (vs SCE), and most preferably more positive than 1.15 V (vs SCE). As for the type of the dye, an azo dye satisfying the above-described requirements is particularly preferred.

The method in general, the specific measuring method and the measuring method used in the present invention for measuring the oxidation potential value (E<sub>ox</sub>) of yellow dye (and also the magenta dye) are the same as those described above for the cyan dye.

The E<sub>ox</sub> value indicates the transferability of an electron from the sample to the electrode and as the value is larger (the oxidation potential is more positive), the electron is less transferable from the sample to the electrode, in other words, the oxidation less occurs. As for the relationship with the structure of compound, the oxidation potential becomes more positive when an electron-withdrawing group is introduced, and becomes more negative



when an electron-donating group is introduced. In the present invention, the oxidation potential is preferably rendered more positive by introducing an electron-withdrawing group into the yellow dye skeleton so as to reduce the reactivity with ozone which is an electrophilic agent.

The dye for use in the present invention preferably has good color hue as well as good fastness, more preferably has a sharp absorption spectrum on the long wavelength side. For this purpose, the yellow dye preferably has  $\lambda_{\text{max}}$  in the region from 390 to 470 nm and a ratio  $I(\lambda_{\text{max}} + 70 \text{ nm})/I(\lambda_{\text{max}})$  of the absorbance at  $\lambda_{\text{max}} + 70 \text{ nm}$  ( $I(\lambda_{\text{max}} + 70 \text{ nm})$ ) to the absorbance at  $\lambda_{\text{max}}$  ( $I(\lambda_{\text{max}})$ ) is preferably 0.2 or less, more preferably 0.1 or less. The lower limit of the ratio is about 0.01. These  $\lambda_{\text{max}}$  and the like are values measured in an aqueous solution of the dye.

The dye satisfying these oxidation potential and absorption properties is preferably a dye represented by the following formula (Y1). However, the compound represented by formula (Y1) is sufficient if the  $\lambda_{\text{max}}$  is in the range from 390 to 470 nm, and the above-described oxidation potential and ratio  $I(\lambda_{\text{max}} + 70 \text{ nm})/I(\lambda_{\text{max}})$  need not be always satisfied.



wherein A<sub>11</sub> and B<sub>11</sub> each independently represents a heterocyclic group which may be substituted.

A heterocyclic ring for the heterocyclic group is preferably a heterocyclic ring constituted by a 5- or 6-membered ring and the heterocyclic ring may have a monocyclic structure or a polycyclic structure resulting from condensation of two or more rings and may be an aromatic heterocyclic ring or a non-aromatic heterocyclic ring. A heteroatom constituting the heterocyclic ring is preferably N, O or S atom.

The heterocyclic ring represented by A<sub>11</sub> in formula (Y1) is preferably 5-pyrazolone, pyrazole, triazole, oxazolone, isoxazolone, barbituric acid, pyridone, pyridine, rhodanine, pyrazolidinedione, pyrazolopyridone, merdramic acid or a condensed heterocyclic ring resulting from condensation of such a heterocyclic ring with a hydrocarbon aromatic ring or a heterocyclic ring, more preferably 5-pyrazolone, 5-aminopyrazole, pyridone, 2,6-diaminopyridine or a pyrazoloazole, still more preferably 5-aminopyrazole, 2-hydroxy-6-pyridone or pyrazolotriazole.

Examples of the heterocyclic group represented by B<sub>11</sub> include pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, pyrrole, indole, furan, benzofuran, thiophene, benzothiophene, pyrazole, imidazole,

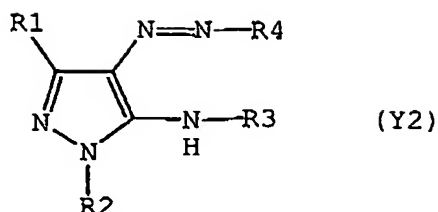
benzimidazole, triazole, oxazole, isoxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, thiadiazole, benzisoxazole, pyrrolidine, piperidine, piperazine, imidazolidine and thiazoline. Among these, preferred are pyridine, quinoline, thiophene, benzothiophene, pyrazole, imidazole, benzimidazole, triazole, oxazole, isoxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, thiadiazole and benzisoxazole, more preferred are quinoline, thiophene, pyrazole, thiazole, benzoxazole, benzisoxazole, isothiazole, imidazole, benzothiazole and thiadiazole, and still more preferred are pyrazole, benzothiazole, benzoxazole, imidazole, 1,2,4-thiadiazole and 1,3,4-thiadiazole.

Examples of the substituent substituted on A<sub>11</sub> and B<sub>11</sub> include a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, an alkoxy group, an aryloxy group, a silyloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group, an acylamino group, an aminocarbonylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfamoylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a mercapto group, an alkylthio group, an arylthio

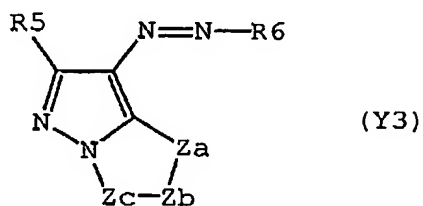
group, a heterocyclic thio group, a sulfamoyl group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an aryloxy carbonyl group, an alkoxycarbonyl group, a carbamoyl group, an imido group, a phosphino group, a phosphinyl group, a phosphinyloxy group, a phosphinylamino group, a silyl group and an ionic hydrophilic group.

In the case where the dye represented by formula (Y1) is used as a water-soluble dye, the dye preferably contains at least one ionic hydrophilic group in the molecule thereof. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, alkali metal salts are preferred.

Among the dyes represented by formula (Y1), preferred are the dyes represented by formulae (Y2), (Y3) and (Y4):

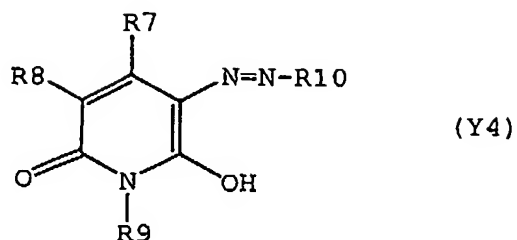


wherein R1 and R3 each represents a hydrogen atom, a cyano group, an alkyl group, a cycloalkyl group, an aralkyl group, an alkoxy group, an alkylthio group, an arylthio group, an aryl group or an ionic hydrophilic group, R2 represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, a carbamoyl group, an acyl group, an aryl group or a heterocyclic group, and R4 represents a heterocyclic group;



wherein R5 represents a hydrogen atom, a cyano group, an alkyl group, a cycloalkyl group, an aralkyl group, an alkoxy group, an alkylthio group, an arylthio group, an aryl group or an ionic hydrophilic group, Za represents -N=, -NH- or -C(R11)=, Zb and Zc each independently represents -N= or -C(R11)=, R11 represents a hydrogen atom

or a nonmetallic substituent, and R6 represents a heterocyclic group;



wherein R7 and R9 each independently represents a hydrogen atom, a cyano group, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group or an ionic hydrophilic group, R8 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, a cyano group, an acylamino group, a sulfonylamino group, an alkoxycarbonylamino group, a ureido group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an amino group, a hydroxy group or an ionic hydrophilic group, and R10 represents a heterocyclic group.

The alkyl group represented by R1, R2, R3, R5, R7, R8 or R9 in formulae (Y2), (Y3) and (Y4) includes an alkyl group having a substituent and an unsubstituted alkyl group. The alkyl group is preferably an alkyl group having from 1

to 20 carbon atoms. Examples of the substituent include a hydroxyl group, an alkoxy group, a cyano group, a halogen atom and an ionic hydrophilic group. Examples of the alkyl group include a methyl group, an ethyl group, a butyl group, an isopropyl group, a tert-butyl group, a hydroxyethyl group, a methoxyethyl group, a cyanoethyl group, a trifluoromethyl group, a 3-sulfopropyl group and a 4-sulfobutyl group.

The cycloalkyl group represented by R1, R2, R3, R5, R7, R8 or R9 includes a cycloalkyl group having a substituent and an unsubstituted cycloalkyl group. The cycloalkyl group is preferably a cycloalkyl group having from 5 to 12 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the cycloalkyl group include a cyclohexyl group.

The aralkyl group represented by R1, R2, R3, R5, R7, R8 or R9 include an aralkyl group having a substituent and an unsubstituted aralkyl group. The aralkyl group is preferably an aralkyl group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aralkyl group include a benzyl group and a 2-phenethyl group.

The aryl group represented by R1, R2, R3, R5, R7, R8 or R9 includes an aryl group having a substituent and an unsubstituted aryl group. The aryl group is preferably an

aryl group having from 6 to 20 carbon atoms. Examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, an alkylamino group and an ionic hydrophilic group. Examples of the aryl group include a phenyl group, a p-tolyl group, a p-methoxyphenyl group, an o-chlorophenyl group and an m-(3-sulfopropylamino)phenyl group.

The alkylthio group represented by R1, R2, R3, R5, R7, R8 or R9 includes an alkylthio group having a substituent and an unsubstituted alkylthio group. The alkylthio group is preferably an alkylthio group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylthio group include a methylthio group and an ethylthio group.

The arylthio group represented by R1, R2, R3, R5, R7, R8 or R9 includes an arylthio group having a substituent and an unsubstituted arylthio group. The arylthio group is preferably an arylthio group having from 6 to 20 carbon atoms. Examples of the substituent include an alkyl group and an ionic hydrophilic group. Examples of the arylthio group include a phenylthio group and a p-tolylthio group.

The heterocyclic group represented by R2 or R<sup>22</sup> which is described later is preferably a 5- or 6-membered heterocyclic ring and the heterocyclic ring may be further condensed. The heteroatom constituting the heterocyclic ring is preferably N, S or O. The ring may be an aromatic



heterocyclic ring or a non-aromatic heterocyclic ring. The heterocyclic ring may be substituted and examples of the substituent are the same as those of the substituent of the aryl group which is described later. The heterocyclic ring is preferably a 6-membered nitrogen-containing aromatic heterocyclic ring and preferred examples thereof include triazine, pyrimidine and phthalazine.

The halogen atom represented by R8 includes a fluorine atom, a chlorine atom and a bromine atom.

The alkoxy group represented by R1, R3, R5 or R8 includes an alkoxy group having a substituent and an unsubstituted alkoxy group. The alkoxy group is preferably an alkoxy group having from 1 to 20 carbon atoms. Examples of the substituent include a hydroxyl group and an ionic hydrophilic group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an isopropoxy group, a methoxyethoxy group, a hydroxyethoxy group and a 3-carboxypropoxy group.

The aryloxy group represented by R8 includes an aryloxy group having a substituent and an unsubstituted aryloxy group. The aryloxy group is preferably an aryloxy group having from 6 to 20 carbon atoms. Examples of the substituent include an alkoxy group and an ionic hydrophilic group. Examples of the aryloxy group include a phenoxy group, a p-methoxyphenoxy group and an o-methoxy-

phenoxy group. The acylamino group represented by R8 includes an acylamino group having a substituent and an unsubstituted acylamino group. The acylamino group is preferably an acylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acylamino group include an acetamide group, a propionamide group, a benzamide group and a 3,5-disulfobenzamide group.

The sulfonylamino group represented by R8 includes a sulfonylamino group having a substituent and an unsubstituted sulfonylamino group. The sulfonylamino group is preferably a sulfonylamino group having from 1 to 20 carbon atoms. Examples of the sulfonylamino group include a methylsulfonylamino group and an ethylsulfonylamino group.

The alkoxycarbonylamino group represented by R8 includes an alkoxycarbonylamino group having a substituent and an unsubstituted alkoxycarbonylamino group. The alkoxycarbonylamino group is preferably an alkoxycarbonylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonylamino group include an ethoxycarbonylamino group.

The ureido group represented by R8 includes a ureido group having a substituent and an unsubstituted ureido group. The ureido group is preferably a ureido group

having from 1 to 20 carbon atoms. Examples of the substituent include an alkyl group and an aryl group. Examples of the ureido group include a 3-methylureido group, a 3,3-dimethylureido group and a 3-phenylureido group.

The alkoxycarbonyl group represented by R7, R8 or R9 includes an alkoxycarbonyl group having a substituent and an unsubstituted alkoxycarbonyl group. The alkoxycarbonyl group is preferably an alkoxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonyl group include a methoxycarbonyl group and an ethoxycarbonyl group.

The carbamoyl group represented by R2, R7, R8 or R9 includes a carbamoyl group having a substituent and an unsubstituted carbamoyl group. Examples of the substituent include an alkyl group. Examples of the carbamoyl group include a methylcarbamoyl group and a dimethylcarbamoyl group.

The sulfamoyl group represented by R8 includes a sulfamoyl group having a substituent and an unsubstituted sulfamoyl group. Examples of the substituent include an alkyl group. Examples of the sulfamoyl group include a dimethylsulfamoyl group and a di-(2-hydroxyethyl)sulfamoyl group.

Examples of the alkylsulfonyl group and arylsulfonyl

group represented by R8 include a methylsulfonyl group and a phenylsulfonyl group.

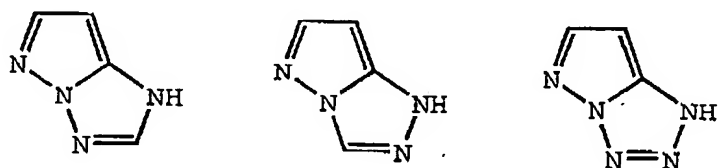
The acyl group represented by R2 or R8 includes an acyl group having a substituent and an unsubstituted acyl group. The acyl group is preferably an acyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyl group include an acetyl group and a benzoyl group.

The amino group represented by R8 includes an amino group having a substituent and an unsubstituted amino group. Examples of the substituent include an alkyl group, an aryl group and a heterocyclic group. Examples of the amino group include a methylamino group, a diethylamino group, an anilino group and a 2-chloroanilino group.

The heterocyclic group represented by R4, R6 or R10 is the same as the heterocyclic group represented by B<sub>11</sub> in formula (Y1), which may be substituted, and preferred examples, more preferred examples and still more preferred examples are the same as those described above. Examples of the substituent include an ionic hydrophilic group, an alkyl group having from 1 to 12 carbon atoms, an aryl group, an alkylthio group, an arylthio group, a halogen atom, a cyano group, a sulfamoyl group, a sulfonamino group, a carbamoyl group and an acylamino group. The alkyl group, the aryl group and the like each may further have a

substituent.

In formula (Y3), Z<sub>a</sub> represents -N=, -NH- or -C(R<sub>11</sub>)=, Z<sub>b</sub> and Z<sub>c</sub> each independently represents -N= or -C(R<sub>11</sub>)=, and R<sub>11</sub> represents a hydrogen atom or a nonmetallic substituent. The nonmetallic substituent represented by R<sub>11</sub> is preferably a cyano group, a cycloalkyl group, an aralkyl group, an aryl group, an alkylthio group, an arylthio group or an ionic hydrophilic group. These substituents have the same meanings as the substituents represented by R<sub>1</sub>, respectively, and preferred examples are also the same. Examples of the skeleton of the heterocyclic ring comprising two 5-membered rings, contained in formula (Y3), are shown below.

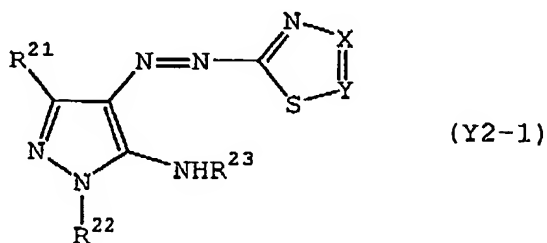


When the above-described substituents each may further have a substituent, examples of the substituent include the substituents which may be substituted to the heterocyclic rings A<sub>11</sub> and B<sub>11</sub> in formula (Y1).

In the case where the dyes represented by formulae (Y2) to (Y4) are used as a water-soluble dye, the dye preferably contains at least one ionic hydrophilic group in

the molecule. In such a case, the dye includes dyes where at least one of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> in formulae (Y<sub>2</sub>) to (Y<sub>4</sub>) is an ionic hydrophilic group, and dyes where R<sub>1</sub> to R<sub>11</sub> in formulae (Y<sub>2</sub>) to (Y<sub>4</sub>) each further has an ionic hydrophilic group as a substituent. The dyes represented by formula (Y<sub>2</sub>) to (Y<sub>4</sub>) each preferably contains an anionic group and as for the number of anionic groups, the dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, per molecule.

Among the dyes represented by formulae (Y<sub>2</sub>), (Y<sub>3</sub>) and (Y<sub>4</sub>), preferred are the dyes represented by formula (Y<sub>2</sub>), and more preferred are the dyes represented by the following formula (Y<sub>2</sub>-1):



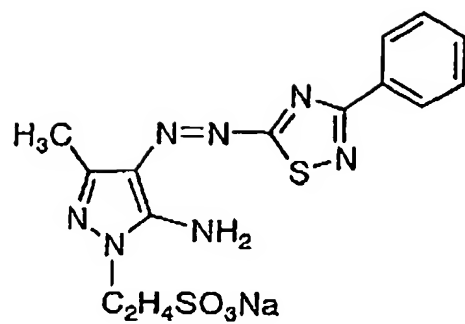
wherein R<sup>21</sup> and R<sup>23</sup> each represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkoxy group or an aryl group, R<sup>22</sup> represents an aryl group or a heterocyclic group, one of X and Y represents a nitrogen atom and another represents -CR<sup>24</sup> (wherein R<sup>24</sup>

represents a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an alkylthio group, an alkylsulfonyl group, an alkylsulfinyl group, an alkyloxycarbonyl group, a carbamoyl group, an alkoxy group, an aryl group, an arylthio group, an arylsulfonyl group, an arylsulfinyl group, an aryloxy group or an acylamino group). The substituents each may be further substituted.

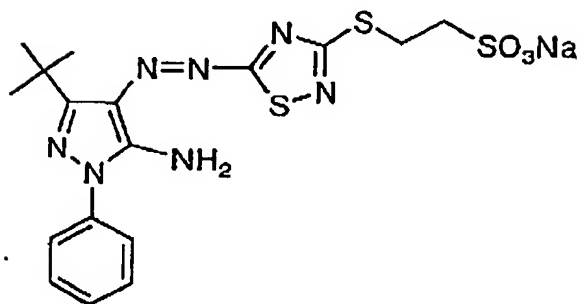
In formula (Y2-1), the dye preferably contains an ionic hydrophilic group, more preferably an anionic group, and as for the number of anionic groups, the dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, per molecule.

Specific examples of preferred dyes for use in the present invention are set forth below, however, the dye for use in the present invention is not limited to the following specific examples. The compounds can be synthesized by referring to JP-A-2-24191 and JP-A-2001-279145.

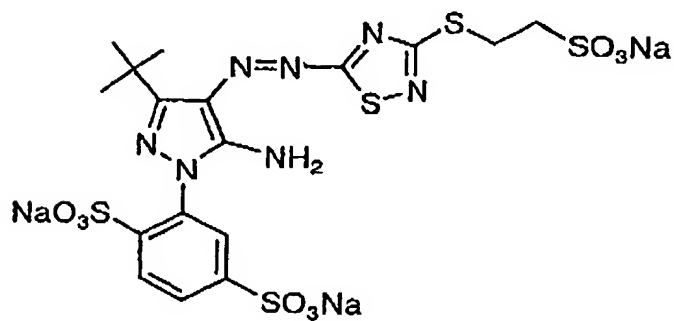
YI-1



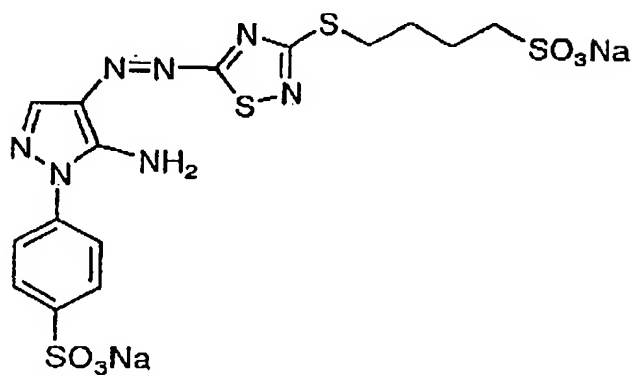
YI-2



YI-3

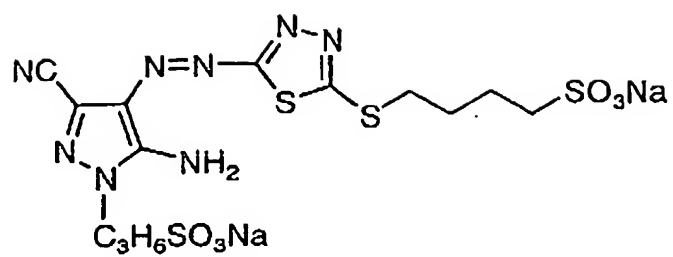


YI-4

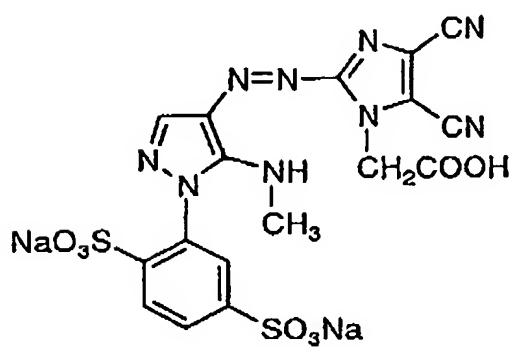




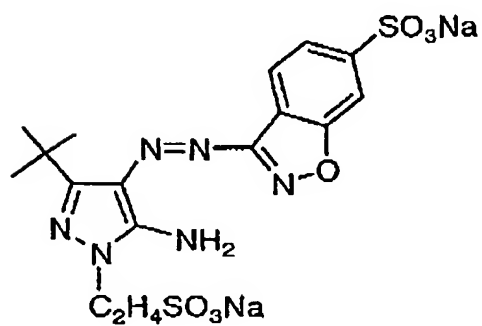
YI-5



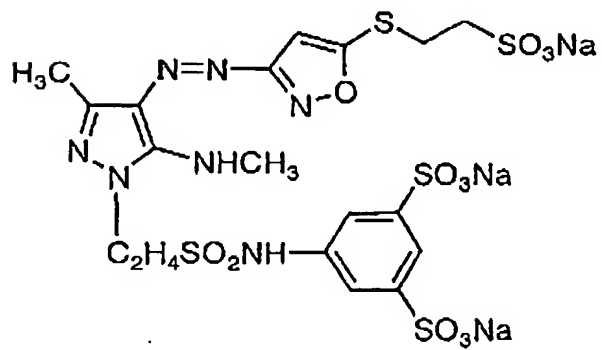
YI-6



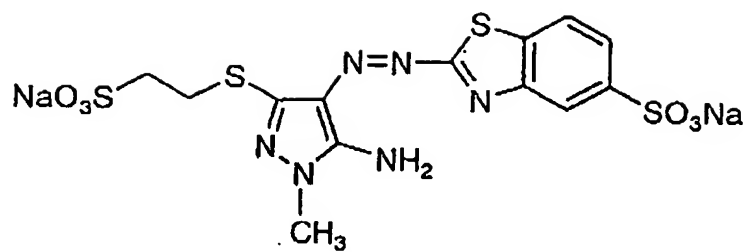
YI-7



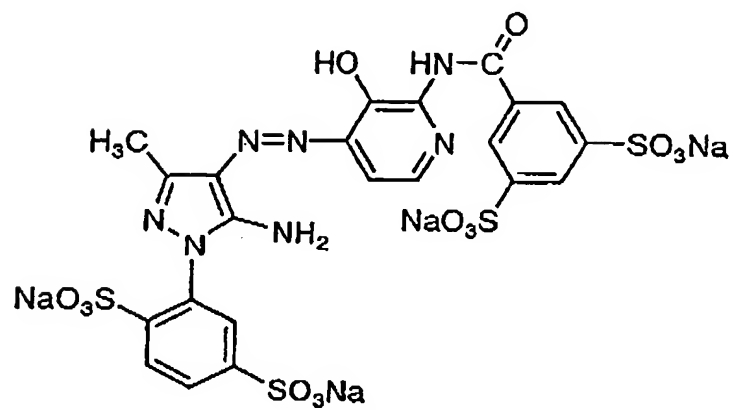
YI-8



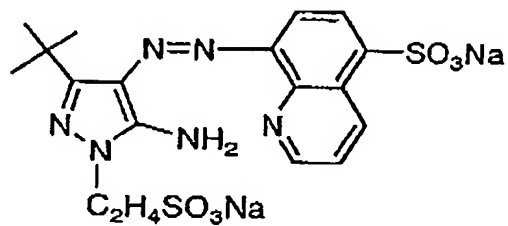
YI-9



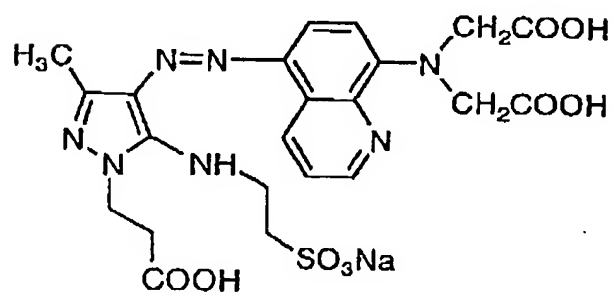
YI-10



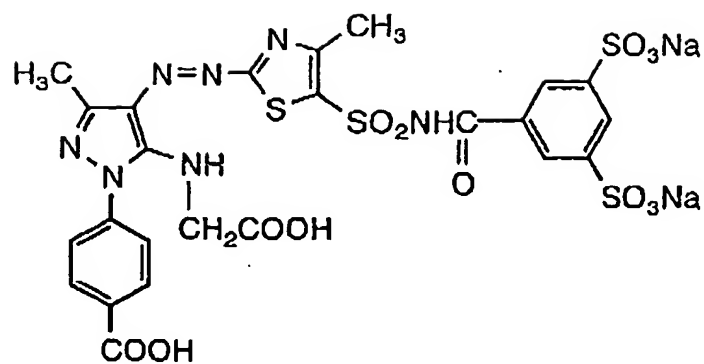
YI-11



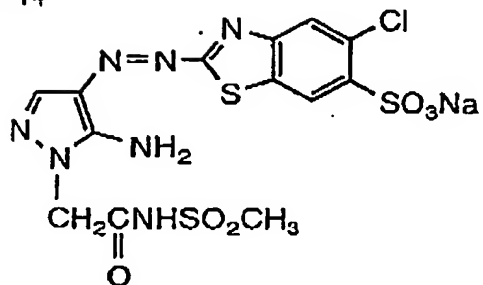
YI-12



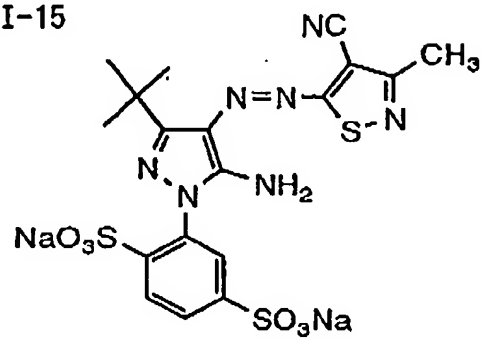
YI-13



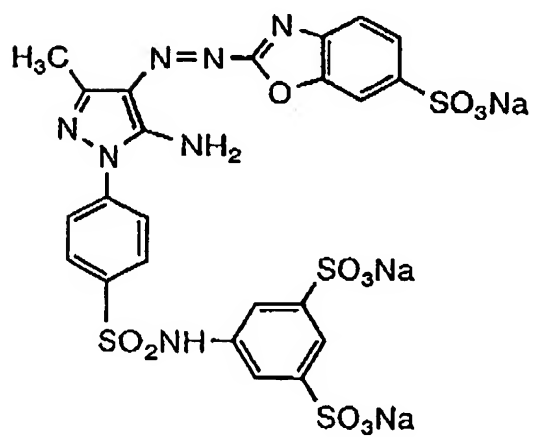
YI-14



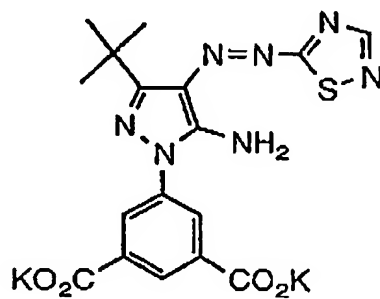
YI-15

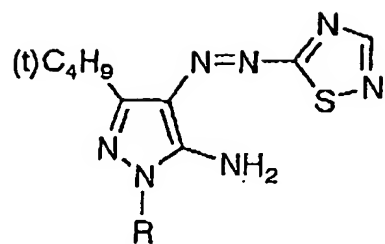


YI-16

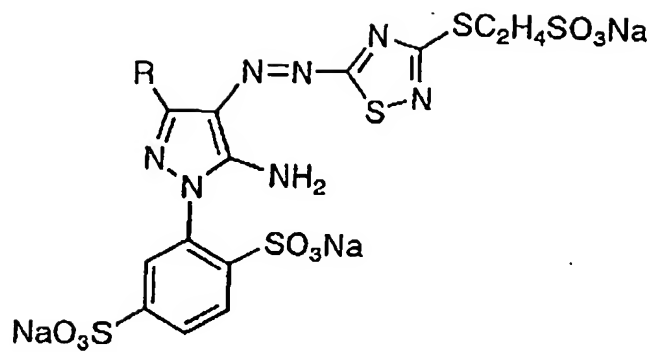


YI-17

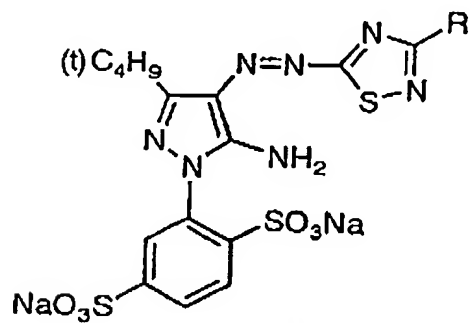




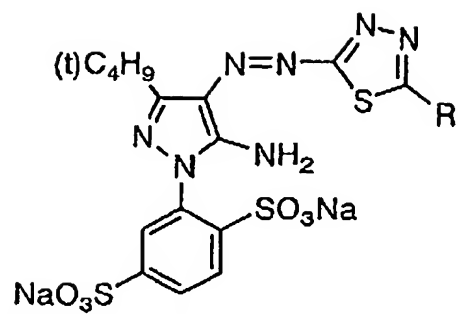
Dye	R
YI-18	CH <sub>3</sub>
YI-19	C <sub>3</sub> H <sub>6</sub> SO <sub>3</sub> Na
YI-20	H
YI-21	C <sub>2</sub> H <sub>4</sub> CN
YI-22	
YI-23	
YI-24	
YI-25	
YI-26	
YI-27	



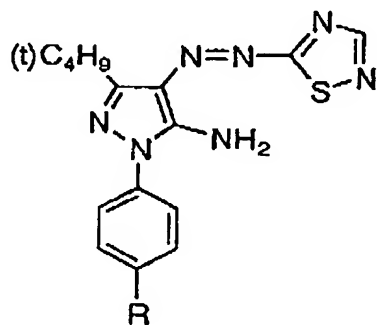
Dye	R
YI-28	CH <sub>3</sub>
YI-29	
YI-30	OC <sub>2</sub> H <sub>5</sub>



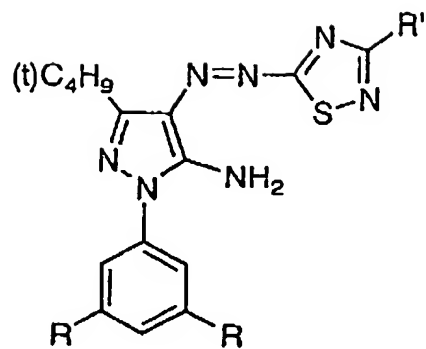
Dye	R
YI-31	
YI-32	CH <sub>3</sub>
YI-33	SC <sub>2</sub> H <sub>4</sub> SO <sub>3</sub> Na
YI-34	SO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> SO <sub>3</sub> Na

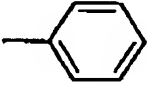
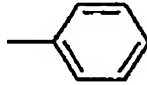


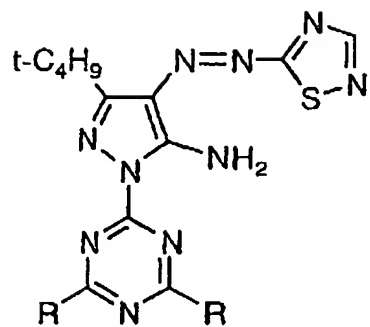
Dye	R
YI-35	H
YI-36	CH <sub>3</sub>
YI-37	



Dye	R
YI-38	COOC <sub>4</sub> H <sub>9</sub>
YI-39	CON(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>
YI-40	SO <sub>2</sub> NHC <sub>12</sub> H <sub>25</sub>
YI-41	OC <sub>8</sub> H <sub>17</sub>

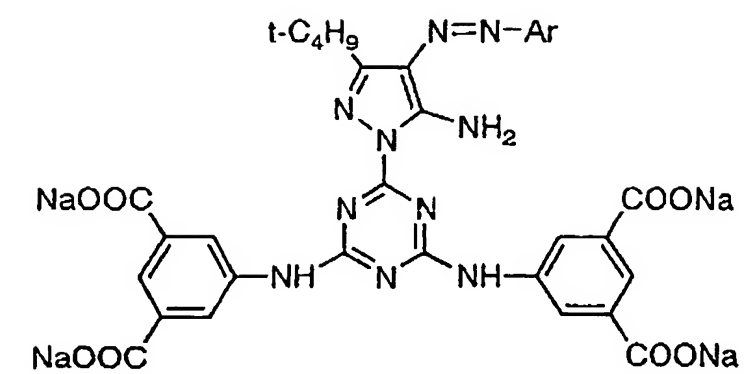


Dye	R	R'
YI-42	CON(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	H
YI-43	COOC <sub>8</sub> H <sub>17</sub>	H
YI-44	CON(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	
YI-45	CON(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	CH <sub>3</sub>
YI-46	H	
YI-47	H	SC <sub>8</sub> H <sub>17</sub>



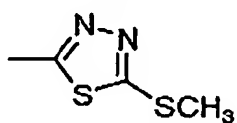
Dye	R
YI-48	$-\text{NHC}_2\text{H}_4\text{COOK}$
YI-49	$-\text{NHC}_2\text{H}_4\text{SO}_3\text{Na}$
YI-50	
YI-51	
YI-52	
YI-53	$-\text{N}(\text{CH}_2\text{COONa})_2$
YI-54	
YI-55	
YI-56	$-\text{NHC}_6\text{H}_{13}$
YI-57	$-\text{N}(\text{C}_4\text{H}_9)_2$



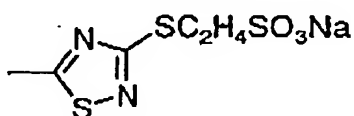


Dye	Ar
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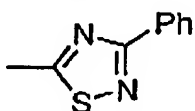
YI-58



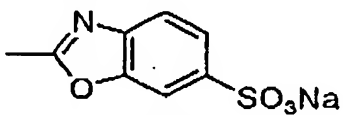
YI-59



YI-60



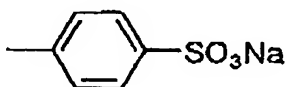
YI-61



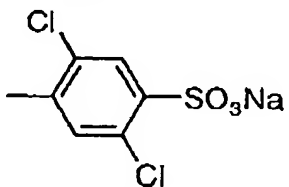
YI-62



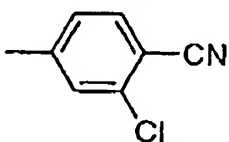
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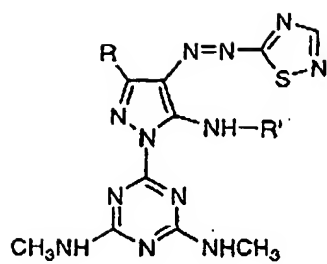


YI-64



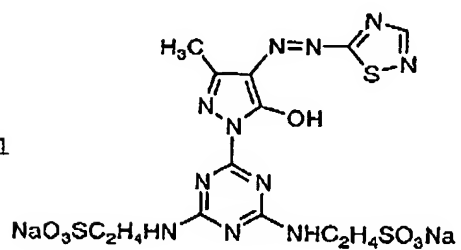
YI-65

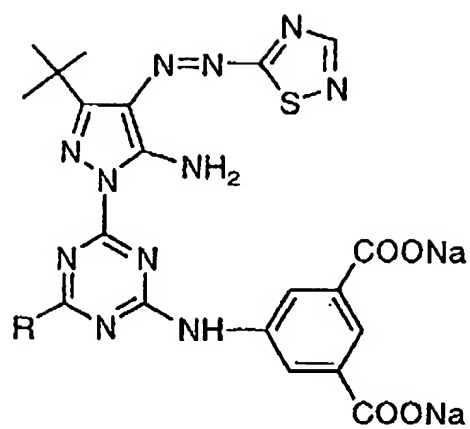




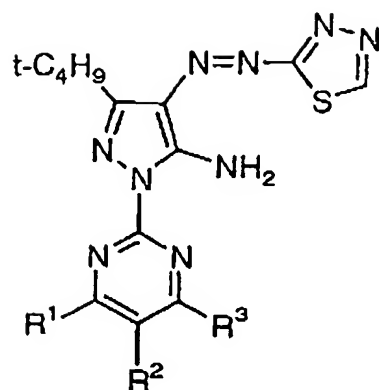
Dye	R	R'
YI-66	Ph	H
YI-67	OC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
YI-68	CH <sub>3</sub>	H
YI-69	t-C <sub>4</sub> H <sub>9</sub>	H
YI-70	t-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>4</sub> COOH

Dye YI-71

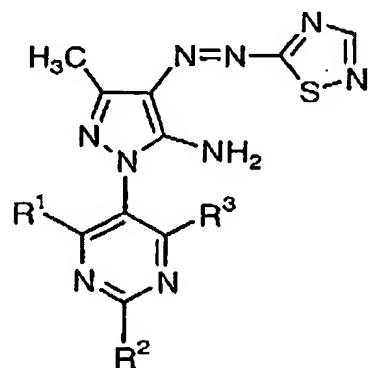




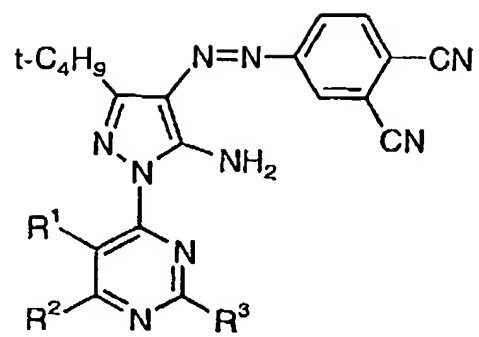
Dye	R
YI-72	H
YI-73	OCH <sub>3</sub>
YI-74	OH
YI-75	SO <sub>3</sub> Na
YI-76	F
YI-77	



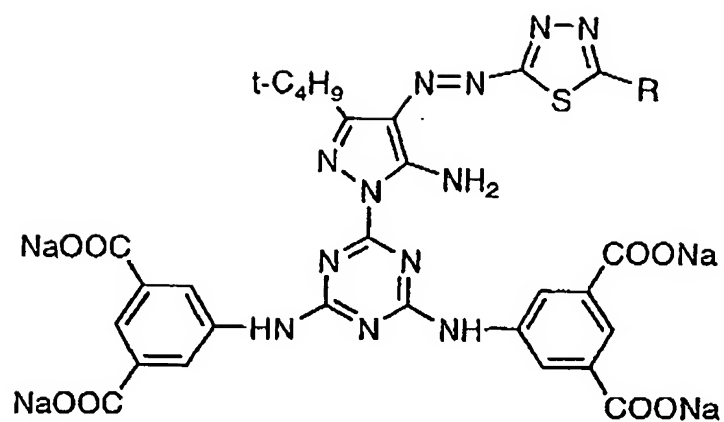
Dye	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
YI-78	Cl	Cl	Cl
YI-79	Cl	Cl	F
YI-80	Cl	-CONHPh	Cl



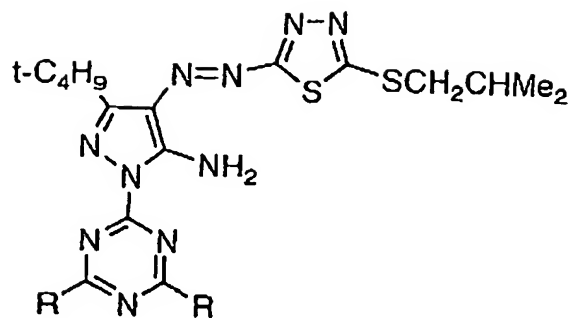
Dye	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
YI-81	F	H	H
YI-82	Cl	H	F



Dye	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
YI-83	H	F	F
YI-84	F	F	H



Dye	R
YI-85	H
YI-86	CH <sub>3</sub>
YI-87	Ph
YI-88	SCH <sub>2</sub> COONa
YI-89	SC <sub>2</sub> H <sub>5</sub>
YI-90	SC <sub>4</sub> H <sub>9-n</sub>
YI-91	SCH <sub>2</sub> CHMe <sub>2</sub>
YI-92	SCHMeEt
YI-93	SC <sub>4</sub> H <sub>9-t</sub>
YI-94	SC <sub>7</sub> H <sub>15-n</sub>
YI-95	SC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>
YI-96	SC <sub>2</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9-n</sub>
YI-97	SCH <sub>2</sub> CF <sub>3</sub>



Dye	R
YI-98	$-\text{NHC}_2\text{H}_4\text{COOK}$
YI-99	$-\text{NHC}_2\text{H}_4\text{SO}_3\text{Na}$
YI-100	
YI-101	
YI-102	
YI-103	
YI-104	$-\text{NHC}_6\text{H}_{13-n}$
YI-105	$-\text{N}(\text{C}_4\text{H}_9-n)_2$
YI-106	$-\text{N}(\text{CH}_2\text{COONa})_2$
YI-107	
YI-108	

The inkjet recording yellow ink preferably contains the yellow dye in an amount of 0.2 to 20 wt%, more preferably from 0.5 to 15 wt%.

[Black Dye]

The black dye for use in the present invention is described in detail below.

In the black ink for inkjet recording of the present invention, a dye (L) having  $\lambda_{\text{max}}$  in the region from 500 to 700 nm and having a half-value width ( $W\lambda_{1/2}$ ) of 100 nm or more (preferably from 120 to 500 nm, more preferably from 120 to 350 nm) in the absorption spectrum of a dilute solution standardized to an absorbance of 1.0 is used.

In the case where the dye (L) by itself can realize black of high image quality "pure black" (that is, black which is not dependent on the light source at the observation and less susceptible to stress of any one color tone of B, G and R), the dye may be used alone as the dye for black ink. However, in general, a dye for covering the region where the dye (L) has low absorption is usually used in combination. A dye (S) having main absorption in the yellow region is preferably used in combination. The black ink may also be produced by using other dyes in combination.

In the present invention, the above-described dye alone or in combination with other dyes is dissolved or dispersed in an aqueous medium to prepare a black ink and



in order to satisfy the performances preferred as the black ink for inkjet recording, namely, 1) the weather resistance is excellent and/or 2) the balance of black is not disrupted even after color fading, an ink satisfying the following conditions is produced.

A black square symbol of JIS code 2223 is printed in a 48-point size by using the black ink and the reflection density ( $D_{vis}$ ) measured by a Status A filter (visual filter) is defined as the initial density. Examples of the reflection densitometer having mounted thereon a Status A filter include X-Rite Densitometer. In the case of measuring the density of "black", the measured value of  $D_{vis}$  is used as the standard observed reflection density. The printed matter is enforcedly discolored by using an ozone discoloration tester capable of always generating 5 ppm of ozone and an accelerated fading rate constant ( $k_{vis}$ ) is determined according the relational formula  $0.8 = \exp(-k_{vis} \cdot t)$  from the time period ( $t$ ) until the reflection density ( $D_{vis}$ ) decreases to 80% of the initial reflection density value.

In the present invention, an ink of giving the accelerated fading rate constant ( $k_{vis}$ ) of  $5.0 \times 10^{-2}$  [hour<sup>-1</sup>] or less, preferably  $3.0 \times 10^{-2}$  [hour<sup>-1</sup>] or less, more preferably  $1.0 \times 10^{-2}$  [hour<sup>-1</sup>] or less, is produced (condition 1).

Also, a black square symbol of JIS code 2223 is printed in a 48-point size by using the black ink and the reflection densities ( $D_R$ ,  $D_G$ ,  $D_B$ ) of three colors of C (cyan), M (magenta) and Y (yellow), which are density values measured by a Status A filter, are defined as the initial densities. The  $D_R$ ,  $D_G$  and  $D_B$  indicate C reflection density by red filter, M reflection density by green filter, and Y reflection density by blue filter, respectively. The printed matter is enforcedly discolored by using an ozone discoloration tester capable of always generating 5 ppm of ozone according to the above-described method and the accelerated fading rate constants ( $k_R$ ,  $k_G$ ,  $k_B$ ) are determined similarly from the time period until the reflection densities ( $D_R$ ,  $D_G$ ,  $D_B$ ) decrease to 80% of respective initial density values. When the ratio (R) of the maximum value to the minimum value in these three accelerated fading rate constants is determined (for example, in the case where  $k_R$  is a maximum value and  $k_G$  is a minimum value,  $R=k_R/k_G$ ), an ink of giving a ratio (R) of 1.2 or less, preferably 1.1 or less, more preferably 1.05 or less, is produced (condition 2).

The "printed matter obtained by printing a black square symbol of JIS code 2223 in a 48-point size" used above is an image printed in a size large enough to cover an aperture of the densitometer and thereby give a

sufficiently large size for the measurement of density.

At least one dye used in the black ink has an oxidation potential more positive than 1.0 V (vs SCE), preferably more positive than 1.1 V (vs SCE), more preferably more positive than 1.15 V (vs SCE), and most preferably more positive than 1.2 V (vs SCE), and at least one of the dyes preferably has  $\lambda_{\text{max}}$  of 500 nm or longer (condition 3).

The oxidation potential used above is a value measured in N,N-dimethylformamide (concentration of compound:  $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ) containing  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  of tetrapropylammonium perchlorate as the supporting electrolyte. In the case of a water-soluble dye, the dye is sometimes hardly dissolved directly in N,N-dimethylformamide. In such a case, the oxidation potential is measured after dissolving the dye by using water in a small amount as much as possible and then diluting it with N,N-dimethylformamide to have a water content of 2% or less.

The oxidation potential value sometimes deviates on the order of several tens of millivolts due to the effect of liquid junction potential, liquid resistance of sample solution, or the like, but the reproducibility of the potential value measured can be guaranteed by calibration using a standard sample (for example, hydroquinone).

The black ink preferably contains the azo dye

represented by formula (BK1) described above. The azo dye represented by formula (BK1) includes those falling under the dye (L) having  $\lambda_{\text{max}}$  in the region from 500 to 700 nm and having a half-value width of 100 nm or more in the absorption spectrum of a dilute solution standardized to an absorbance of 1.0. Further, a dye (S) having  $\lambda_{\text{max}}$  in the region from 350 to 500 nm is also included in the dye represented by formula (BK1). An ink where at least one dye (L) is the dye of formula (BK1) is preferred, an ink where at least one dye (L) and at least one dye (S) are the dyes of formula (BK1) is more preferred, and an ink where 90 wt% of all dyes in the ink is occupied by the dye of formula (BK1) is still more preferred (condition 4).

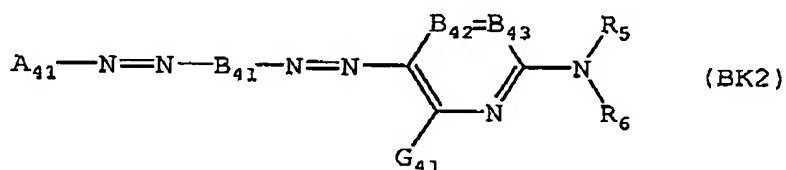
The black ink which can be used in the present invention is a black ink satisfying at least one of these conditions 1 to 4.

Of the dyes represented by formula (BK1), the dye falling under the dye (L) is described in detail below.

In formula (BK1),  $A_{41}$ ,  $B_{41}$  and  $C_{41}$  each independently represents an aromatic group which may be substituted or a heterocyclic group which may be substituted ( $A_{41}$  and  $C_{41}$  each is a monovalent group and  $B_{41}$  is a divalent group),  $m$  represents 1 or 2, and  $n$  represents an integer of 0 or more, preferably an integer of 0 to 10, and more preferably an integer of 0 to 5.

A compound where m and n each is 1 or 2 is preferred and in such a case, at least two of A<sub>41</sub>, B<sub>41</sub> and C<sub>41</sub> are preferably an unsaturated heterocyclic group which may be substituted. In particular, a compound where m and n are 1 and at least B<sub>41</sub> and C<sub>41</sub> are each an unsaturated heterocyclic group is more preferred.

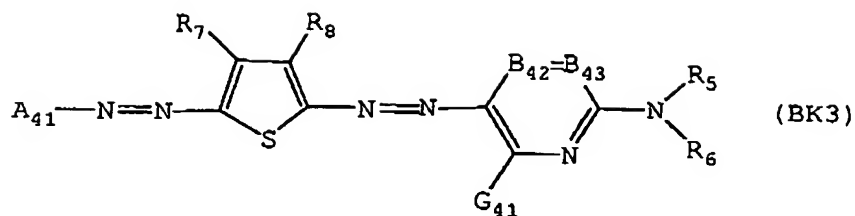
The azo dye represented by formula (BK1) is preferably a dye represented by the following formula (BK2):



wherein A<sub>41</sub> and B<sub>41</sub> have the same meanings as defined in formula (BK1), respectively; B<sub>42</sub> and B<sub>43</sub> each represents =CR<sub>1</sub>- or -CR<sub>2</sub>= or either one of B<sub>41</sub> and B<sub>42</sub> represents a nitrogen atom and the other represents =CR<sub>1</sub>- or -CR<sub>2</sub>=; G<sub>41</sub>, R<sub>1</sub> and R<sub>2</sub> each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an

acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and each group may be further substituted;  $R_5$  and  $R_6$  each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent, provided that  $R_5$  and  $R_6$  are not hydrogen atoms at the same time; or  $R_1$  and  $R_5$ , or  $R_5$  and  $R_6$  may combine to form a 5- or 6-membered ring.

The azo dye represented by formula (BK2) is more preferably a dye represented by the following formula (BK3):



wherein  $R_7$  and  $R_8$  each has the same meaning as  $R_1$  in formula (BK2).

The halogen atom includes a fluorine atom, a chlorine atom and a bromine atom. The aliphatic group means an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an aralkyl group and a substituted aralkyl group. The aliphatic group may be branched or may form a ring. The number of carbon atoms in the aliphatic group is preferably from 1 to 20, more preferably from 1 to 16. The aryl moiety in the aralkyl group and the substituted aralkyl group is preferably phenyl or naphthyl, more preferably phenyl. Examples of the aliphatic group include a methyl group, an ethyl group, a butyl group, an isopropyl group, a tert-butyl group, a hydroxyethyl group, a methoxyethyl group, a cyanoethyl group, a trifluoromethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a cyclohexyl group, a benzyl group, a 2-phenethyl group, a vinyl group and an allyl group.

The monovalent aromatic group means an aryl group and

a substituted aryl group. The aryl group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. The number of carbon atoms in the monovalent aromatic group is preferably from 6 to 20, more preferably from 6 to 16. Examples of the monovalent aromatic group include a phenyl group, a p-tolyl group, a p-methoxyphenyl group, an o-chlorophenyl group and an m-(3-sulfopropylamino)phenyl group. The divalent aromatic group is a divalent form of these monovalent aromatic groups and examples thereof include a phenylene group, a p-tolylene group, a p-methoxyphenylene group, an o-chlorophenylene group, an m-(3-sulfopropylamino)phenylene group and a naphthylene group.

The heterocyclic group includes a heterocyclic group having a substituent and an unsubstituted heterocyclic group. The heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or other heterocyclic ring. The heterocyclic group is preferably a 5-membered or 6-membered heterocyclic group. Examples of the heteroatom in the heterocyclic ring include N, O and S. Examples of the substituent include an aliphatic group, a halogen atom, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfamoyl group, a carbamoyl group and an ionic hydrophilic group. Examples of the heterocyclic ring used in the monovalent or divalent heterocyclic



group include a pyridine ring, a thiophene ring, a thiazole ring, a benzothiazole ring, a benzoxazole ring and a furan ring.

The carbamoyl group includes a carbamoyl group having a substituent and an unsubstituted carbamoyl group. Examples of the substituent include an alkyl group. Examples of the carbamoyl group include a methylcarbamoyl group and a dimethylcarbamoyl group.

The alkoxycarbonyl group includes an alkoxycarbonyl group having a substituent and an unsubstituted alkoxycarbonyl group. The alkoxycarbonyl group is preferably an alkoxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonyl group include a methoxycarbonyl group and an ethoxycarbonyl group.

The aryloxy carbonyl group includes an aryloxy carbonyl group having a substituent and an unsubstituted aryloxy carbonyl group. The aryloxy carbonyl group is preferably an aryloxy carbonyl group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aryloxy carbonyl group include a phenoxycarbonyl group.

The heterocyclic oxycarbonyl group includes a heterocyclic oxycarbonyl group having a substituent and an unsubstituted heterocyclic oxycarbonyl group. The

heterocyclic oxycarbonyl group is preferably a heterocyclic oxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic oxycarbonyl group include a 2-pyridyloxycarbonyl group.

The acyl group includes an acyl group having a substituent and an unsubstituted acyl group. The acyl group is preferably an acyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyl group include an acetyl group and a benzoyl group.

The alkoxy group includes an alkoxy group having a substituent and an unsubstituted alkoxy group. The alkoxy group is preferably an alkoxy group having from 1 to 20 carbon atoms. Examples of the substituent include an alkoxy group, a hydroxyl group and an ionic hydrophilic group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an isopropoxy group, a methoxyethoxy group, a hydroxyethoxy group and a 3-carboxypropoxy group.

The aryloxy group includes an aryloxy group having a substituent and an unsubstituted aryloxy group. The aryloxy group is preferably an aryloxy group having from 6 to 20 carbon atoms. Examples of the substituent include an alkoxy group and an ionic hydrophilic group. Examples of

the aryloxy group include a phenoxy group, a p-methoxyphenoxy group and an o-methoxyphenoxy group.

The heterocyclic oxy group includes a heterocyclic oxy group having a substituent and an unsubstituted heterocyclic oxy group. The heterocyclic oxy group is preferably a heterocyclic oxy group having from 2 to 20 carbon atoms. Examples of the substituent include an alkyl group, an alkoxy group and an ionic hydrophilic group. Examples of the heterocyclic oxy group include a 3-pyridyloxy group and a 3-thienyloxy group.

The silyloxy group is preferably a silyloxy group substituted by an aliphatic or aromatic group having from 1 to 20 carbon atoms. Examples of the silyloxy group include a trimethylsilyloxy group and a diphenylmethylsilyloxy group.

The acyloxy group includes an acyloxy group having a substituent and an unsubstituted acyloxy group. The acyloxy group is preferably an acyloxy group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyloxy group include an acetoxy group and a benzoyloxy group.

The carbamoyloxy group includes a carbamoyloxy group having a substituent and an unsubstituted carbamoyloxy group. Examples of the substituent include an alkyl group. Examples of the carbamoyloxy group include an N-methyl-

carbamoyloxy group.

The alkoxycarbonyloxy group includes an alkoxycarbonyloxy group having a substituent and an unsubstituted alkoxycarbonyloxy group. The alkoxycarbonyloxy group is preferably an alkoxycarbonyloxy group having from 2 to 20 carbon atoms. Examples of the alkoxycarbonyloxy group include a methoxycarbonyloxy group and an isopropoxycarbonyloxy group.

The aryloxcarbonyloxy group includes an aryloxcarbonyloxy group having a substituent and an unsubstituted aryloxcarbonyloxy group. The aryloxcarbonyloxy group is preferably an aryloxcarbonyloxy group having from 7 to 20 carbon atoms. Examples of the aryloxcarbonyloxy group include a phenoxycarbonyloxy group.

The amino group includes an amino group substituted by an alkyl group, an aryl group or a heterocyclic group, and the alkyl group, the aryl group and the heterocyclic group each may further have a substituent. The alkylamino group is preferably an alkylamino group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylamino group include a methylamino group and a diethylamino group.

The arylamino group includes an arylamino group having a substituent and an unsubstituted arylamino group. The arylamino group is preferably an arylamino group having

from 6 to 20 carbon atoms. Examples of the substituent include a halogen atom and an ionic hydrophilic group. Examples of the arylamino group include an anilino group and a 2-chlorophenylamino group.

The heterocyclic amino group includes a heterocyclic amino group having a substituent and an unsubstituted heterocyclic amino group. The heterocyclic amino group is preferably a heterocyclic amino group having from 2 to 20 carbon atoms. Examples of the substituent include an alkyl group, a halogen atom and an ionic hydrophilic group.

The acylamino group includes an acylamino group having a substituent and an unsubstituted acylamino group. The acylamino group is preferably an acylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acylamino group include an acetylamino group, a propionylamino group, a benzoylamino group, an N-phenylacetylamino group and a 3,5-disulfobenzoylamino group.

The ureido group includes a ureido group having a substituent and an unsubstituted ureido group. The ureido group is preferably a ureido group having from 1 to 20 carbon atoms. Examples of the substituent include an alkyl group and an aryl group. Examples of the ureido group include a 3-methylureido group, a 3,3-dimethylureido group and a 3-phenylureido group.

The sulfamoylamino group includes a sulfamoylamino group having a substituent and an unsubstituted sulfamoylamino group. Examples of the substituent include an alkyl group. Examples of the sulfamoylamino group include an N,N-dipropylsulfamoylamino group.

The alkoxycarbonylamino group includes an alkoxycarbonylamino group having a substituent and an unsubstituted alkoxycarbonylamino group. The alkoxycarbonylamino group is preferably an alkoxycarbonylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonylamino group include an ethoxycarbonylamino group.

The aryloxy carbonylamino group includes an aryloxy carbonylamino group having a substituent and an unsubstituted aryloxy carbonylamino group. The aryloxy carbonylamino group is preferably an aryloxy carbonylamino group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aryloxy carbonylamino group include a phenoxy carbonylamino group.

The alkylsulfonylamino group includes an alkylsulfonylamino group having a substituent and an unsubstituted alkylsulfonylamino group, and the arylsulfonylamino group includes an arylsulfonylamino group

having a substituent and an unsubstituted arylsulfonylamino group. The sulfonylamino group is preferably a sulfonylamino group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of these sulfonylamino groups include a methylsulfonylamino group, an N-phenyl-methylsulfonylamino group, a phenylsulfonylamino group and a 3-carboxyphenylsulfonylamino group.

The heterocyclic sulfonylamino group includes a heterocyclic sulfonylamino group having a substituent and an unsubstituted heterocyclic sulfonylamino group. The heterocyclic sulfonylamino group is preferably a heterocyclic sulfonylamino group having from 1 to 12 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfonylamino group include a 2-thiophenesulfonylamino group and a 3-pyridinesulfonylamino group.

The heterocyclic sulfonyl group includes a heterocyclic sulfonyl group having a substituent and an unsubstituted heterocyclic sulfonyl group. The heterocyclic sulfonyl group is preferably a heterocyclic sulfonyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfonyl group include a 2-thiophenesulfonyl group and a 3-pyridinesulfonyl group.

The heterocyclic sulfinyl group includes a heterocyclic sulfinyl group having a substituent and an unsubstituted heterocyclic sulfinyl group. The heterocyclic sulfinyl group is preferably a heterocyclic sulfinyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfinyl group include a 4-pyridine-sulfinyl group.

The alkylthio group includes include an alkylthio group having a substituent and an unsubstituted alkylthio group, the arylthio group includes an arylthio group having a substituent and an unsubstituted arylthio group, and the heterocyclic thio group includes a heterocyclic thio group having a substituent and an unsubstituted heterocyclic thio group. The alkylthio group, the arylthio group and the heterocyclic thio group are preferably an alkylthio group having from 1 to 20 carbon atoms, an arylthio group having from 1 to 20 carbon atoms and a heterocyclic thio group having from 1 to 20 carbon atoms, respectively. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylthio group, arylthio group and heterocyclic thio group include a methylthio group, a phenylthio group and a 2-pyridylthio group.

The alkylsulfonyl group includes an alkylsulfonyl group having a substituent and an unsubstituted



alkylsulfonyl group, and the arylsulfonyl group includes an arylsulfonyl group having a substituent and an unsubstituted arylsulfonyl group. Examples of the alkylsulfonyl group and arylsulfonyl group include a methylsulfonyl group and a phenylsulfonyl group.

The alkylsulfinyl group includes an alkylsulfinyl group having a substituent and an unsubstituted alkylsulfinyl group, and the arylsulfinyl group includes an arylsulfinyl group having a substituent and an unsubstituted arylsulfinyl group. Examples of the alkylsulfinyl group and arylsulfinyl group include a methylsulfinyl group and a phenylsulfinyl group.

The sulfamoyl group includes a sulfamoyl group having a substituent and an unsubstituted sulfamoyl group. Examples of the substituent include an alkyl group. Examples of the sulfamoyl group include a dimethylsulfamoyl group and a di-(2-hydroxyethyl)sulfamoyl group.

Formulae (BK1), (BK2) and (BK3) are described in detail below.

In the following, those described above for each group or substituent are also applied.

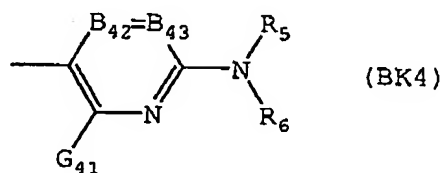
In formula (BK1),  $A_{41}$ ,  $B_{41}$  and  $C_{41}$  each independently represents an aromatic group ( $A_{41}$  and  $C_{41}$  are a monovalent aromatic group such as aryl group, and  $B_{41}$  is a divalent aromatic group such as arylene group) which may be

substituted, or a heterocyclic group ( $A_{41}$  and  $C_{41}$  each is a monovalent heterocyclic group and  $B_{41}$  is a divalent heterocyclic group) which may be substituted. Examples of the aromatic ring include a benzene ring and a naphthalene ring. Examples of the heteroatom in the heterocyclic ring include N, O and S. The heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or other heterocyclic ring.

The substituent may be an arylazo group or a heterocyclic azo group.

At least two of  $A_{41}$ ,  $B_{41}$  and  $C_{41}$  are preferably a heterocyclic group.

The heterocyclic group represented by  $C_{41}$  is preferably an aromatic nitrogen-containing 6-membered heterocyclic group represented by the following formula (BK4). When  $C_{41}$  is an aromatic nitrogen-containing 6-membered heterocyclic group represented by formula (BK4), formula (BK1) corresponds to formula (BK2).



In formula (BK4),  $B_{41}$  and  $B_{42}$  each represents  $=CR_1-$  or  $-CR_2=$  or either one of  $B_{42}$  and  $B_{43}$  represents a nitrogen

atom and the other represents  $=CR_1-$  or  $-CR_2=$ .  $B_{42}$  and  $B_{43}$  each is preferably  $=CR_1-$  or  $-CR_2=$ .

$R_5$  and  $R_6$  each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent. The substituent represented by  $R_5$  and  $R_6$  is preferably a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group, and each group may further have a substituent. However,  $R_5$  and  $R_6$  are not hydrogen atoms at the same time.

$G_{41}$ ,  $R_1$  and  $R_2$  each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy

group, an aryloxy-carbonyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxy-carbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and each group may be further substituted.

The substituent represented by  $G_{41}$  is preferably a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a hydroxyl group, an alkoxy group, an aryloxy group, an acyloxy group, a heterocyclic oxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxy-carbonylamino group, an alkylthio group, an arylthio group or a heterocyclic thio group, more preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group)

or an acylamino group, and most preferably a hydrogen atom, an anilino group or an acylamino group, and each group may further have a substituent.

The substituents represented by  $R_1$  and  $R_2$  each is preferably a hydrogen atom, an alkyl group, a halogen atom, an alkoxy carbonyl group, a carboxyl group, a carbamoyl group, a hydroxy group, an alkoxy group or a cyano group, and each group may further have a substituent.

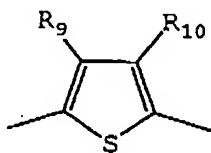
$R_1$  and  $R_5$ , or  $R_5$  and  $R_6$  may combine to form a 5-membered or 6-membered ring. When the substituents represented by  $A_{41}$ ,  $R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$  and  $G_{41}$  each further has a substituent, examples of the substituent include the substituents described above for  $G_{41}$ ,  $R_1$  and  $R_2$ . Also, an ionic hydrophilic group is preferably further present as a substituent on any one position of  $A_{41}$ ,  $R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$  and  $G_{41}$ .

Examples of the ionic hydrophilic group as a substituent include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium

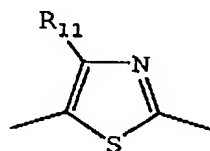
ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium).

When  $B_{41}$  has a ring structure, preferred examples of the heterocyclic ring include a thiophene ring, a thiazole ring, an imidazole ring, a benzothiazole ring and a thienothiazole ring. Each heterocyclic group may further have a substituent. Among these heterocyclic rings, a thiophene ring, a thiazole ring, an imidazole ring, a benzothiazole ring and a thienothiazole ring represented by the following formulae (a) to (e) respectively are preferred. When  $m=n=1$ ,  $B_{41}$  is a thiophene ring represented by formula (a), and  $C_{41}$  is a structure represented by formula (4), formula (BK1) corresponds to formula (BK3).

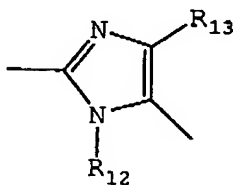
(a)



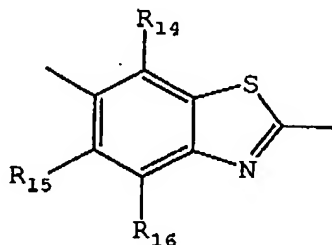
(b)



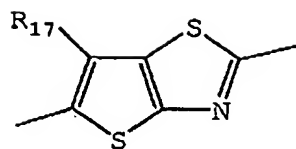
(c)



(d)

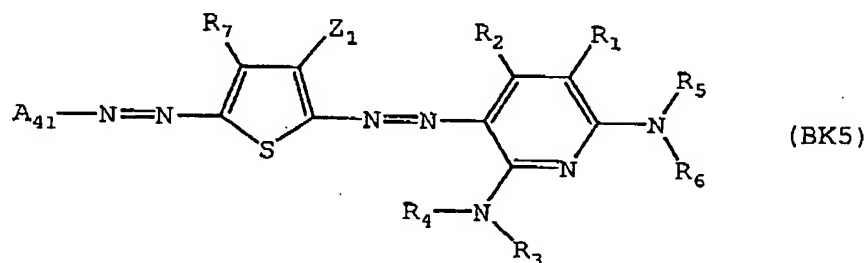


(e)



wherein  $R_9$  to  $R_{17}$  each represents a substituent having the same meaning as  $G_{41}$ ,  $R_1$  and  $R_2$  in formula (BK2).

In the present invention, particularly preferred is a structure represented by the following formula (BK5):



In formula (BK5),  $Z_1$  represents an electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.20 or more.  $Z_1$  is preferably an electron-withdrawing group having a  $\sigma_p$  value of 0.30 or more, more preferably 0.45 or more, still more preferably 0.60 to more, but the  $\sigma_p$  value preferably does not exceed 1.0. Specific preferred examples of this substituent include electron-withdrawing substituents described later. Among those,

preferred are an acyl group having from 2 to 20 carbon atoms, an alkyloxycarbonyl group having from 2 to 20 carbon atoms, a nitro group, a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, an arylsulfonyl group having from 6 to 20 carbon atoms, a carbamoyl group having from 1 to 20 carbon atoms and a halogenated alkyl group having from 1 to 20 carbon atoms, more preferred are a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms and an arylsulfonyl group having from 6 to 20 carbon atoms, and most preferred is a cyano group.

$R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$  and  $R_7$  have the same meanings as in formula (BK2).  $R_3$  and  $R_4$  each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group or a heterocyclic group.

The groups described in regard to formula (BK5) each may further have a substituent. When these groups each further has a substituent, examples of the substituent include the substituents described in regard to formula (BK2), the groups described as examples for  $G_{41}$ ,  $R_1$  and  $R_2$ ,



and ionic hydrophilic groups.

Now, the Hammett's substituent constant  $\sigma_p$  value used in the present invention is described. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a  $\sigma_p$  value and a  $\sigma_m$  value and these values can be found in a large number of conventional publications and these are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979). In the present invention, each substituent is limited or described by using the Hammett's substituent constant  $\sigma_p$ , but it does not mean that the substituent is limited only to those having a known value which can be found in the above-described publications. Needless to say, the substituent includes substituents of which  $\sigma_p$  value is not known in publications but when measured based on the Hammett's rule, falls within the range specified.

Examples of the electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.60 or more include a cyano group, a nitro group, an alkylsulfonyl

group (e.g., methanesulfonyl) and an arylsulfonyl group (e.g., benzenesulfonyl).

Examples of the electron-withdrawing group having a Hammett's  $\sigma_p$  value of 0.45 or more include, in addition to those described above, an acyl group (e.g., acetyl), an alkoxycarbonyl group (e.g., dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., m-chlorophenoxycarbonyl), an alkylsulfinyl group (e.g., n-propylsulfinyl), an arylsulfinyl group (e.g., phenylsulfinyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl) and a halogenated alkyl group (e.g., trifluoromethyl).

Examples of the electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.30 or more include, in addition to those described above, an acyloxy group (e.g., acetoxy), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a halogenated alkoxy group (e.g., trifluoromethyloxy), a halogenated aryloxy group (e.g., pentafluorophenyloxy), a sulfonyloxy group (e.g., methylsulfonyloxy), a halogenated alkylthio group (e.g., difluoromethylthio), an aryl group substituted by two or more electron-withdrawing groups having a  $\sigma_p$  value of 0.15 or more (e.g., 2,4-dinitrophenyl, pentachlorophenyl) and a heterocyclic ring (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl).

Specific examples of the electron-withdrawing group

having a  $\sigma_p$  value of 0.20 or more include, in addition to those described above, a halogen atom.

The preferred combination of substituents in the azo dye represented by formula (BK3) is described below.  $R_5$  and  $R_6$  each is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a sulfonyl group or an acyl group, more preferably a hydrogen atom, an aryl group, a heterocyclic group or a sulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group. However,  $R_5$  and  $R_6$  are not a hydrogen atom at the same time.

$G_{41}$  is preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an amino group or an acylamino group, more preferably a hydrogen atom, a halogen atom, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group or an acylamino group.

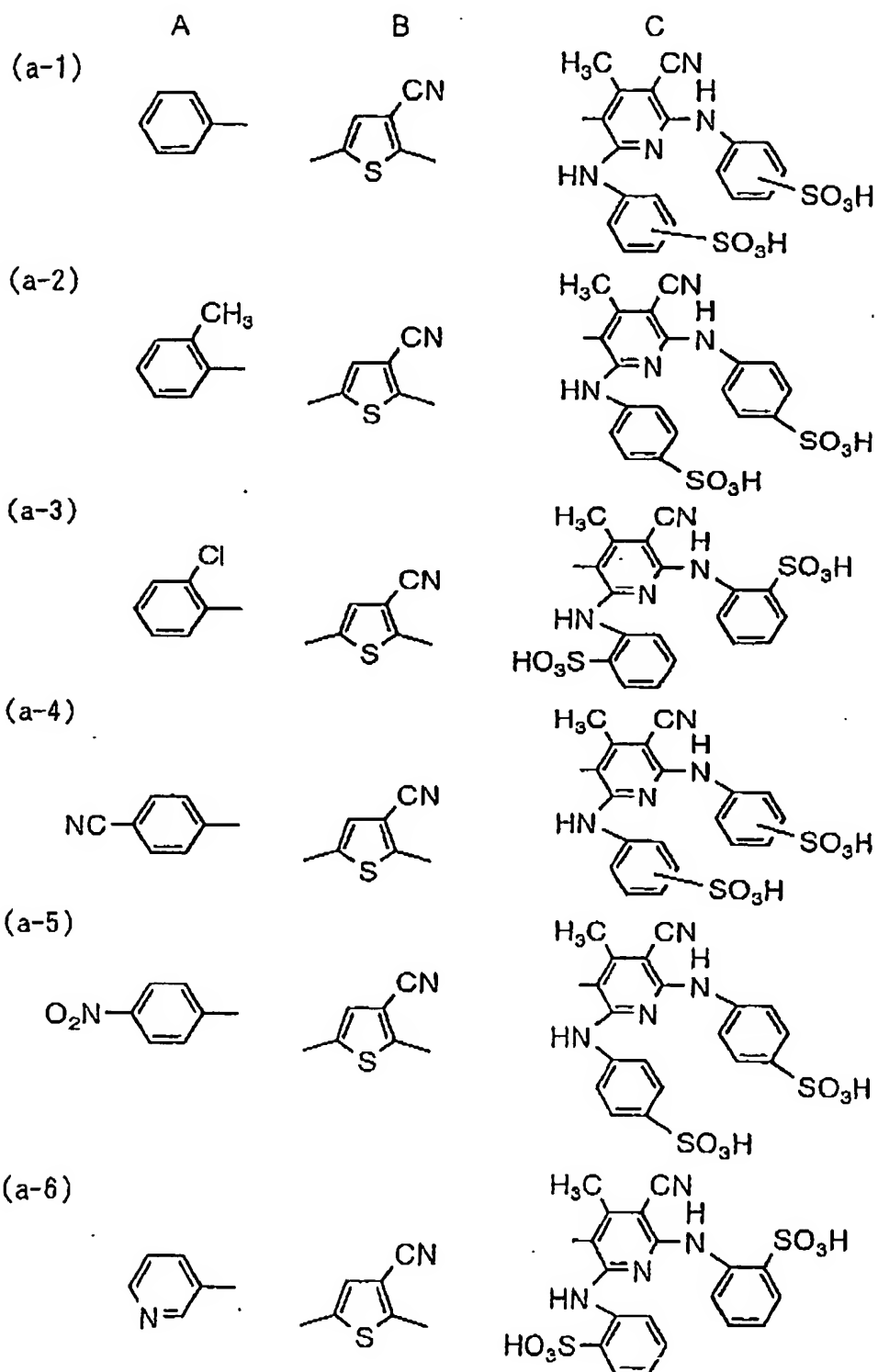
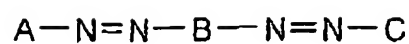
$A_{41}$  is preferably an aromatic group, a pyridine ring, a pyrazole ring, an imidazole ring, an isothiazole ring, a benzisothiazole ring, a thiadiazole ring, a thiazole ring, a benzothiazole ring or a triazole ring, more preferably an aromatic group, a pyridine ring, an isothiazole ring, a benzisothiazole ring, a thiadiazole ring or a benzothiazole ring, and most preferably an aromatic group, a pyridine ring or a benzothiazole ring.

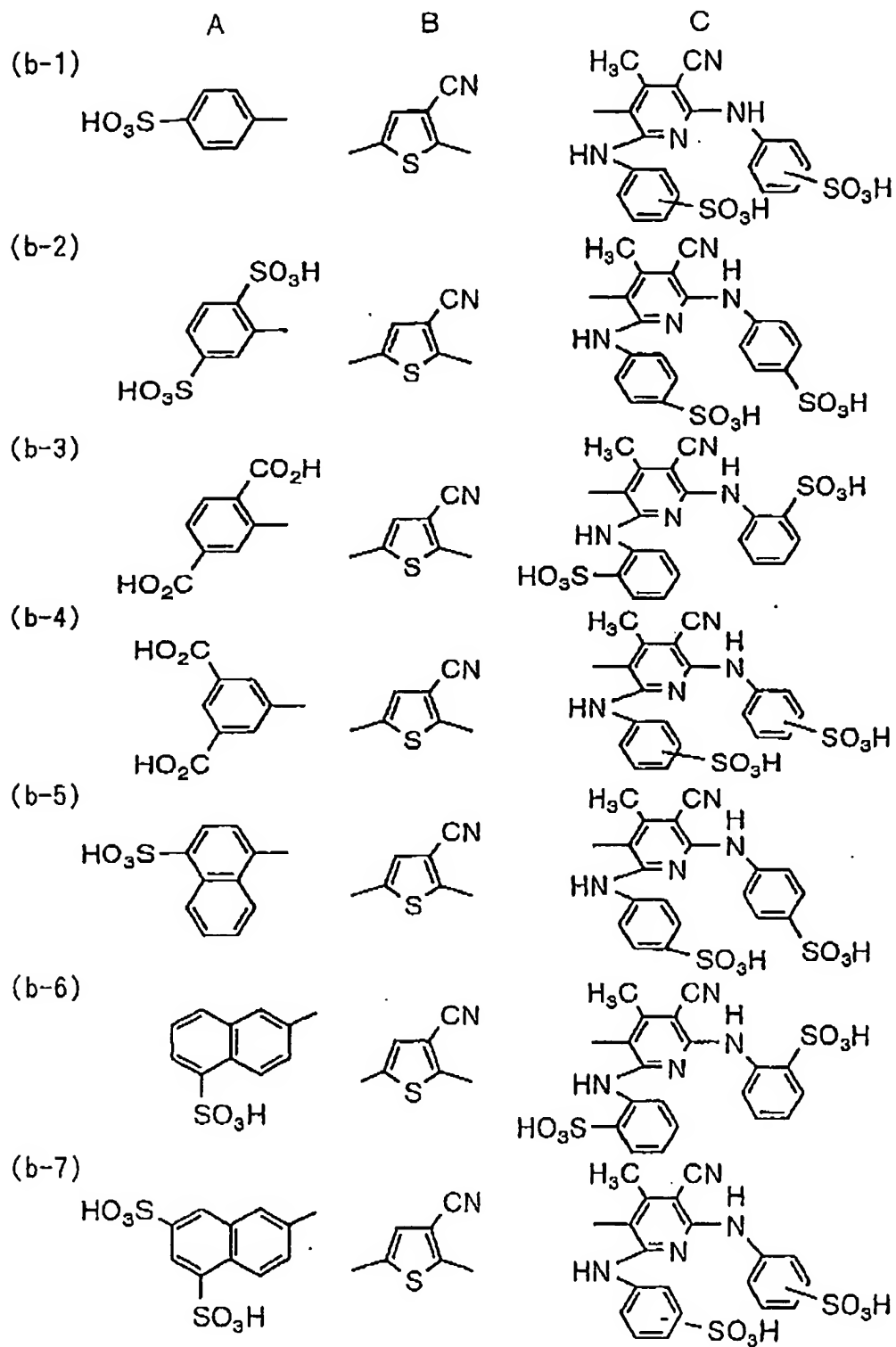
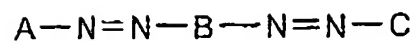
B<sub>41</sub> and B<sub>42</sub> each is =CR<sub>1</sub>- or -CR<sub>2</sub>=, and R<sub>1</sub> and R<sub>2</sub> each is preferably a hydrogen atom, an alkyl group, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, a hydroxyl group, an alkoxy group or an alkoxycarbonyl group, more preferably a hydrogen atom, an alkyl group, a carboxyl group, a cyano group or a carbamoyl group.

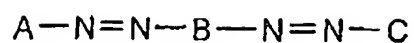
As for the preferred combination of substituents in the compound represented by formula (BK1), a compound where at least one of various substituents is the above-described preferred group is preferred, a compound where a larger number of various substituents are the above-described preferred groups is more preferred, and a compound where all substituents are the above-described preferred groups is most preferred. The dye represented by formula (BK1) preferably contains an anionic group and as for the number of anionic groups, the dye preferably contains at least two anionic groups, more preferably at least two sulfo groups and/or carboxyl groups, per molecule.

Specific examples of the azo dye represented by formula (BK1) are set forth below, however, the azo dye for use in the present invention is not limited to those set forth below. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium

ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium).





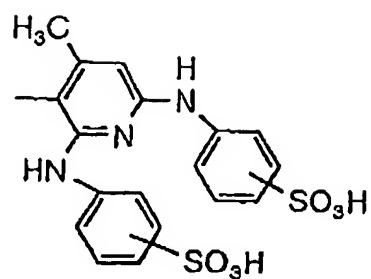
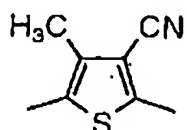
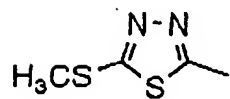


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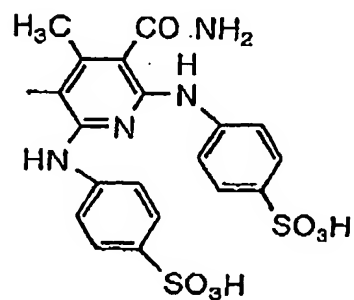
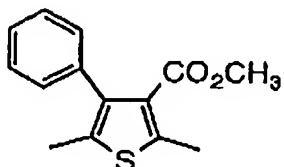
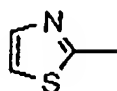
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C

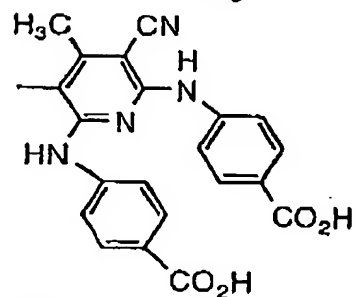
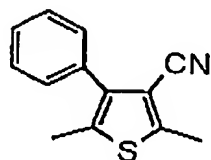
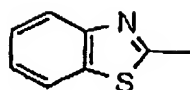
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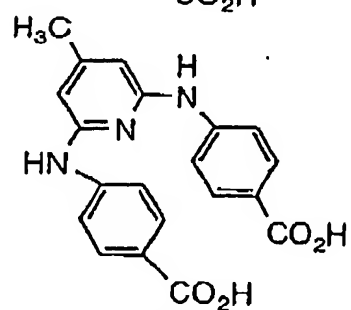
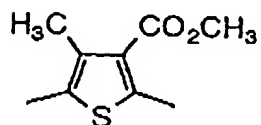
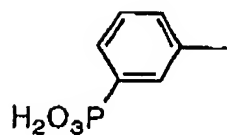
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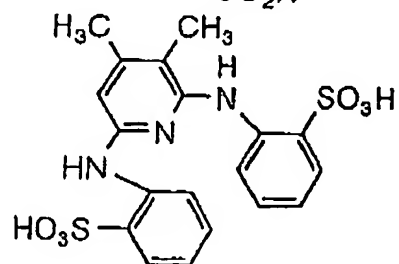
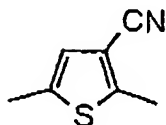
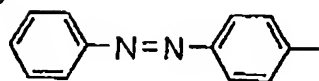
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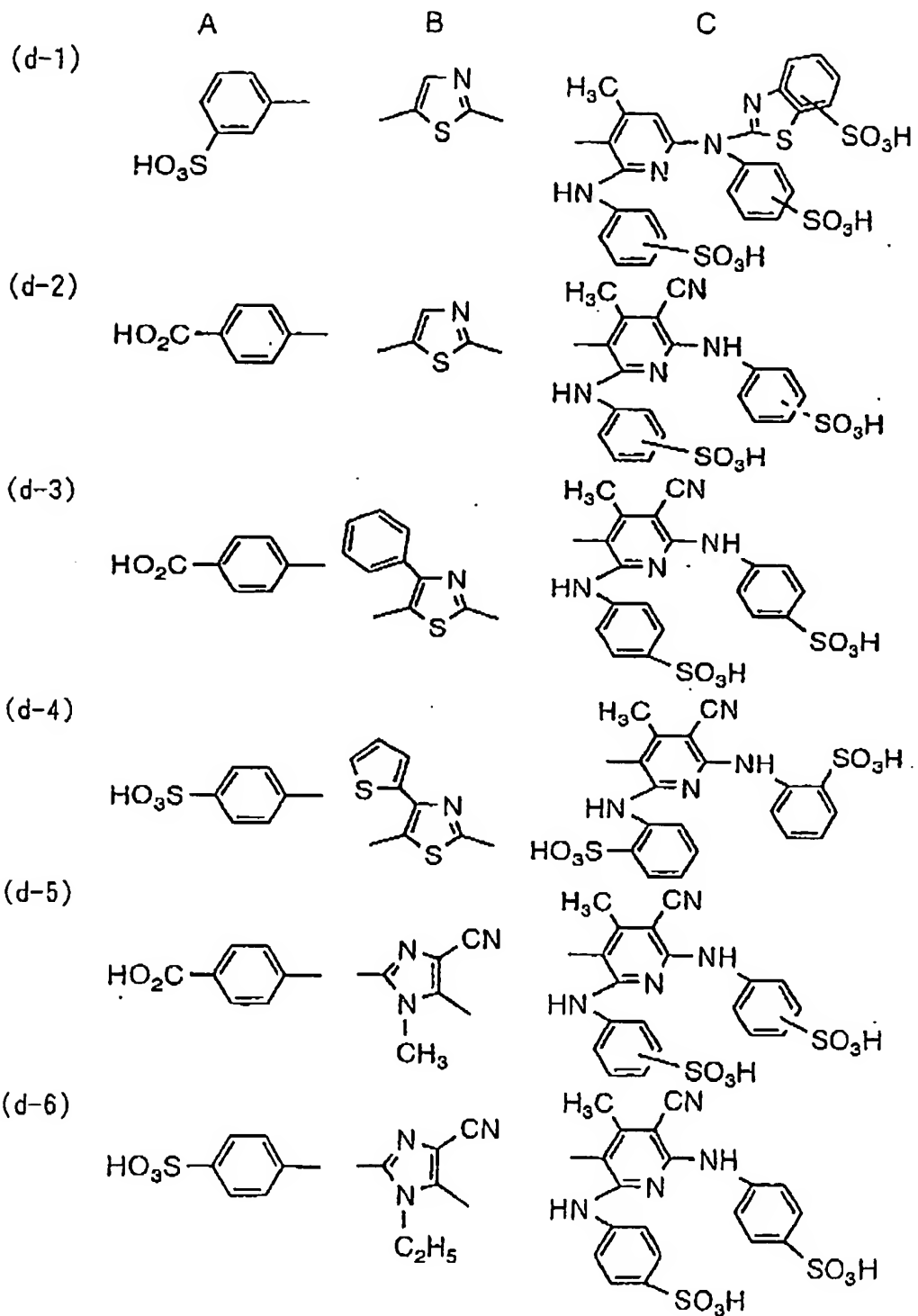
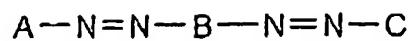
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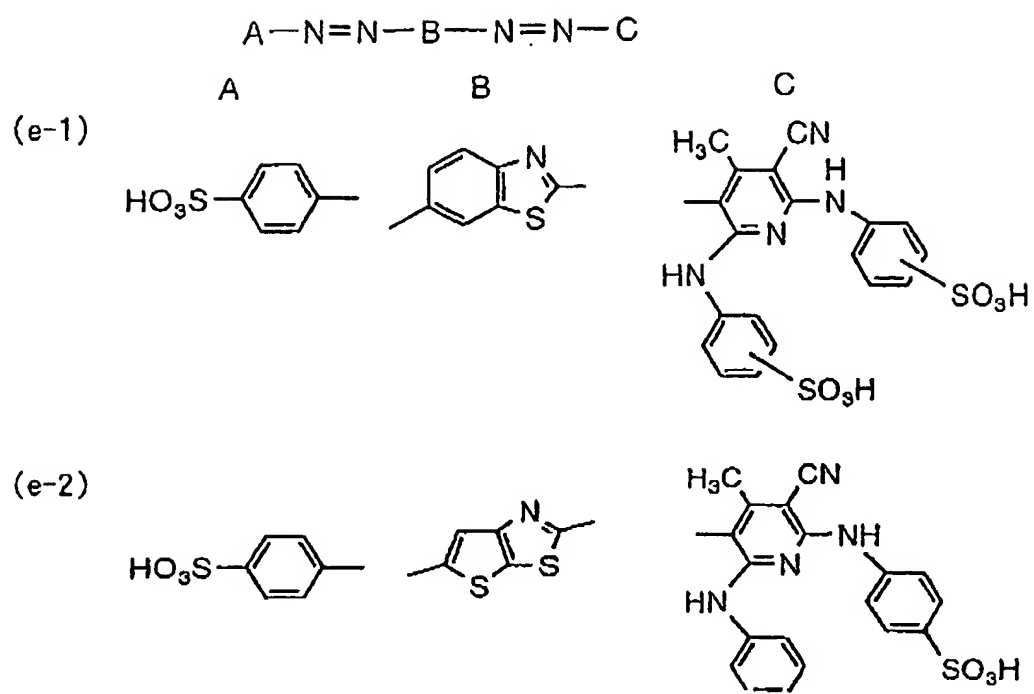


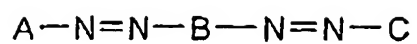
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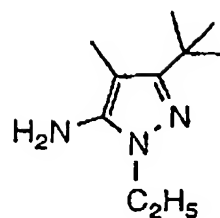
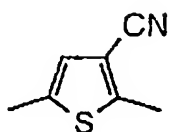
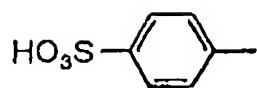


A

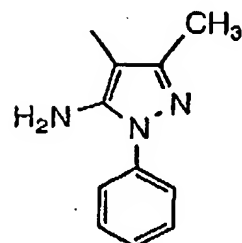
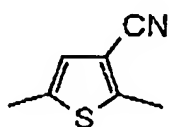
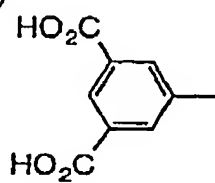
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C

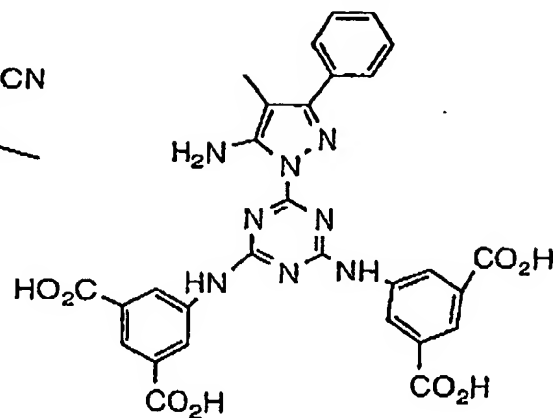
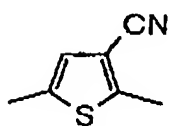
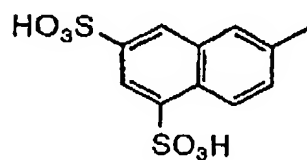
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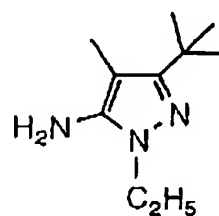
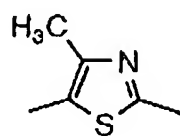
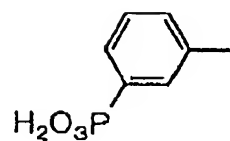
(f-2)



(f-3)



(f-4)



The dyes represented by formulae (BK1), (BK2), (BK3) and (BK5) can be synthesized by a coupling reaction of a diazo component and a coupler. As the main synthesis method, the method described in JP-A-2003-306623 can be used.

In the case where the dye (L) by itself can realize black of high image quality "pure black" (that is, black which is not dependent on the light source at the observation and less susceptible to stress of any one color tone of B, G and R), the dye may be used alone as the dye for black ink. However, in general, a dye for covering the region where the dye (L) has low absorption is usually used in combination. A dye or pigment having main absorption in the yellow region is usually used in combination to realize the preferred black. As the yellow dye, commonly employed direct dyes, acid dyes and the like, representatively azo dyes and azomethine dyes, can be used. As the pigment, an aqueous dispersion of a conventional pigment having a pigment number can be used in combination. In particular, a dye represented by formula (BK1) as the short-wave dye (S) described above is preferably used.

Among the dyes represented by formula (BK1), an azo dye where  $m=n=0$  is firstly preferred as the short-wave dye (S). In such a case,  $A_{41}$  and  $C_{41}$  each is preferably a heteroaromatic ring. An azo dye where  $m=n=1$  is next

preferred.

In either case, the dye preferably has an oxidation potential ( $E_{ox}$ ) of more positive than 1.0 V (vs SCE), more preferably more positive than 1.15 V (vs SCE).

In the black ink, at least two long-wavelength dyes can be also used in combination.

Furthermore, the black ink can be also produced by using other dyes in combination.

The black ink for inkjet recording according to the present invention contains the dye of formula (BK1) in an amount of 0.2 to 25 wt%, preferably from 0.5 to 15 wt%, based on the entire ink.

For the dye having  $\lambda_{max}$  in the region from 350 to 500 nm, a yellow dye or pigment described later can be also used.

The above-described black dye is substantially soluble or dispersible in water. In particular, the ink composition containing the black dye of the present invention is preferably a solution-type ink composition using a water-soluble dye. More specifically, the solubility of the dye in water at 20°C is preferably 2 wt% or more, more preferably 5 wt% or more.

The dyes other than the black dye for use in the present invention are preferably a substantially water-soluble or water-dispersible dye. More specifically, the

solubility of the dye in water at 20°C is preferably 2 wt% or more, more preferably 5 wt% or more.

In the case of producing two or more inks, one ink may be produced as a light-type thin ink and another may be produced as a thick ink. In the present invention, such inks can be produced. Further, ink compositions which provide almost the same printed density can be produced.

Examples of the dye which can be used other than the above-described black dye include dyes known in the field of art, such as triarylmethane dye, anthraquinone dye, anthrapyridone dye, azomethine dye, azo dye, cyanine dye, merocyanine dye and oxonol dye, and these dyes can be used individually or in combination (preferably in combination of giving a black dye). Among these, azo dyes are preferred.

More specifically, examples of the yellow dye include aryl- or heteryl-azo dyes having a phenol, a naphthol, an aniline, a pyrazolone, a pyridone or an open chain active methylene compound as the coupling component; azomethine dyes having an open chain active methylene compound as the coupling component; methine dyes such as benzylidene dye and monomethine oxonol dye; and quinone-base dyes such as naphthoquinone dye and anthraquinone dye. Other examples of the dye species include quinophthalone dye, nitro-nitroso dye, acridine dye and acridinone dye. Such a

dye may be a dye which provides a yellow color for the first time when a part of the chromophore is dissociated. In such a case, a counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure.

Examples of the magenta dye include aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; azomethine dyes having a pyrazolone or a pyrazolotriazole as the coupling component; methine dyes such as arylidene dye, styryl dye, merocyanine dye and oxonol dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; quinone-base dyes such as naphthoquinone, anthraquinone and anthrapyridone; and condensed polycyclic dyes such as dioxazine dye. These dyes may be those which provide a magenta color for the first time when a part of the chromophore is dissociated. In such a case, a counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure.

Examples of the cyan dye include azomethine dyes such as indoaniline dye and indophenol dye; polymethine dyes such as cyanine dye, oxonol dye and merocyanine dye; carbonium dyes such as diphenylmethane dye,

triphenylmethane dye and xanthene dye; phthalocyanine dyes; anthraquinone dyes; aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; and indigo-thioindigo dyes. These dyes may be those which provide a cyan color for the first time when a part of the chromophore is dissociated. In such a case, a counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure.

Examples of the water-soluble dye includes a direct dye, an acid dye, a food dye, a basic dye and a reactive dye. Preferred examples thereof include C.I. Direct Red 2, 4, 9, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 21, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243 and 247; C.I. Direct Violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100 and 101; C.I. Direct Yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161 and 163; C.I. Direct Blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76, 77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 151, 156, 158, 159, 160, 168, 189, 192, 193, 194, 199, 200, 201, 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237, 244, 248, 249, 251, 252, 264, 270, 280, 288, 289 and 291; C.I.



Direct Black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77, 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122, 125, 132, 146, 154, 166, 168, 173 and 199; C.I. Acid Red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 151, 154, 158, 249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396 and 397; C.I. Acid Violet 5, 34, 43, 47, 48, 90, 103 and 126; C.I. Acid Yellow 17, 19, 23, 25, 39, 40, 42, 44, 49, 50, 61, 64, 76, 79, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222 and 227; C.I. Acid Blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82, 92, 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205, 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277, 278, 279, 280, 288, 290 and 326; C.I. Acid Black 7, 24, 29, 48, 52:1 and 172; C.I. Reactive Red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49 and 55; C.I. Reactive Violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33 and 34; C.I. Reactive Yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41 and 42; C.I. Reactive Blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29 and 38; C.I. Reactive Black 4, 5, 8, 14, 21, 23, 26, 31, 32 and 34; C.I. Basic Red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45 and 46; C.I. Basic Violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40 and 48; C.I. Basic Yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39 and 40; C.I. Basic

Blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69 and 71; and C.I. Basic Black 8.

In the ink set of the present invention, other dyes may be used in combination with the above-described dyes so as to adjust the color tone for obtaining a full color image. Examples of the dye which can be used in combination include the dyes described above and the following pigments.

As the pigment which can be used in the present invention, commercially available pigments and known pigments described in various publications can be used. Examples of the publication include Colour Index, compiled by The Society of Dyers and Colourists, Kaitei Shin Han Ganryo Binran (Revised New Handbook of Pigments), compiled by Nippon Ganryo Gijutsu Kyokai (1989), Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Publishing Co., Ltd. (1986), Insatsu Ink Gijutsu (Printing Ink Technique), CMC Publishing Co., Ltd. (1984), and W. Herbst and K. Hunger, Industrial Organic Pigments, VCH Verlagsgesellschaft (1993). Specific examples of the pigment include organic pigments such as azo pigments (e.g., azo lake pigment, insoluble azo pigment, condensed azo pigment, chelate azo pigment), polycyclic pigments (e.g., phthalocyanine-base pigment, anthraquinone-base pigment, perylene-base or perynone-base pigment, indigo-base pigment,

quinacridone-base pigment, dioxazine-base pigment, isoindolinone-base pigment, quinophthalone-base pigment, diketopyrrolopyrrole-base pigment), dyeing lake pigments (lake pigments of acidic or basic dye) and azine pigments, and inorganic pigments such as C.I. Pigment Yellow 34, 37, 42 and 53 which are a yellow pigment, C.I. Pigment Red 101 and 108 which are a red-type pigment, C.I. Pigment Blue 27, 29 and 17:1 which are a blue-type pigment, C.I. Pigment Black 7 and magnetite which are a black-type pigment, and C.I. Pigment White 4, 6, 18 and 21 which are a white-type pigment.

The pigment having a color tone preferred for the formation of an image includes the followings. As the blue to cyan pigment, phthalocyanine pigments, anthraquinone-type indanthrone pigments (for example, C.I. Pigment Blue 60) and dyeing lake pigment-type triarylcarbonium pigments are preferred, and phthalocyanine pigments are most preferred (preferred examples thereof include copper phthalocyanine such as C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4 and 15:6, monochloro or low chlorinated copper phthalocyanine, aluminum phthalocyanine such as pigments described in European Patent 860475, nonmetallic phthalocyanine such as C.I. Pigment Blue 16, and phthalocyanine with the center metal being Zn, Ni or Ti, and among these, C.I. Pigment Blue 15:3 and 15:4 and

aluminum phthalocyanine are more preferred).

As the red to violet pigment, azo pigments (preferred examples thereof include C.I. Pigment Red 3, 5, 11, 22, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 52:1, 53:1, 57:1, 63:2, 144, 146 and 184, and among these, C.I. Pigment Red 57:1, 146 and 184 are more preferred), quinacridone-base pigments (preferred examples thereof include C.I. Pigment Red 122, 192, 202, 207 and 209 and C.I. Pigment Violet 19 and 42, and among these, C.I. Pigment Red 122 is more preferred), dyeing lake pigment-type triarylcarbonium pigments (preferred examples thereof include xanthene-base C.I. Pigment Red 81:1 and C.I. Pigment Violet 1, 2, 3, 27 and 39), dioxazine-base pigments (for example, C.I. Pigment Violet 23 and 37), diketopyrrolopyrrole-base pigments (for example, C.I. Pigment Red 254), perylene pigments (for example, C.I. Pigment Violet 29), anthraquinone-base pigments (for example, C.I. Pigment Violet 5:1, 31 and 33) and thioindigo-base pigments (for example, C.I. Pigment Red 38 and 88) are preferred.

As the yellow pigment, azo pigments (preferred examples thereof include monoazo pigment-type C.I. Pigment Yellow 1, 3, 74 and 98, disazo pigment-type C.I. Pigment Yellow 12, 13, 14, 16, 17 and 83, synthetic azo-type C.I. Pigment Yellow 93, 94, 95, 128 and 155, and benzimidazolone-type C.I. Pigment Yellow 120, 151, 154, 156

and 180, and among these, those not using a benzidine-base compound as a raw material are more preferred), isoindoline-isoindolinone-base pigments (preferred examples thereof include C.I. Pigment Yellow 109, 110, 137 and 139), quinophthalone pigments (preferred examples thereof include C.I. Pigment Yellow 138) and flavanthrone pigments (for example, C.I. Pigment Yellow 24) are preferred.

As the black pigment, inorganic pigments (preferred examples thereof include carbon black and magnetite) and aniline black are preferred.

Other than these, an orange pigment (for example, C.I. Pigment Orange 13 and 16) and a green pigment (for example, C.I. Pigment Green 7) may be used.

The pigment which can be used in the present invention may be the above-described pigment which is not subjected to any treatment or is subjected to a surface treatment. For the surface treatment, a method of coating the surface with resin or wax, a method of attaching a surfactant, and a method of binding a reactive substance (for example, a radical generated from a silane coupling agent, an epoxy compound, polyisocyanate or a diazonium salt) to the pigment surface may be used and these are described in the following publications and patents:

- (1) Kinzoku Sekken no Seishitsu to Oyo (Properties and Applications of Metal Soap), Saiwai Shobo Co., Ltd.;

(2) Insatsu Ink Insatsu (Printing Ink Printing),  
CMC Publishing Co., Ltd. (1984);

(3) Saishin Ganryo Oyo Gijutsu (Newest Pigment  
Application Technology), CMC Publishing Co., Ltd. (1986);

(4) U.S. Patents 5,554,739 and 5,571,311; and

(5) JP-A-9-151342, JP-A-10-140065, JP-A-10-292143  
and JP-A-11-166145.

Particularly, self-dispersible pigments prepared by allowing a diazonium salt to act on carbon black described in U.S. Patents of (4) and capsulated pigments prepared by the method described in JP-As of (5) are effective, because dispersion stability can be obtained without using an excess dispersant in the ink.

In the ink of the present invention, the pigment may be dispersed by further using a dispersant. Various known dispersants can be used according to the pigment used, for example, a surfactant-type low molecular dispersant or a polymer-type dispersant can be used. Examples of the dispersant include those described in JP-A-3-69949 and European Patent 549486. In case of using the dispersant, a pigment derivative called synergist may also be added so as to accelerate the adsorption of dispersant to the pigment.

The particle size of the pigment which can be used in the present invention is, after the dispersion, preferably from 0.01 to 10  $\mu\text{m}$ , more preferably from 0.05 to 1  $\mu\text{m}$ .

As for the method of dispersing the pigment, known dispersion techniques used for the production of ink or toner can be used. Examples of the dispersing machine include vertical or horizontal agitator mill, attritor, colloid mill, ball mill, three-roll mill, pearl mill, super-mill, impeller, disperser, KD mill, dynatron and pressure kneader. These are described in detail in Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Publishing Co., Ltd. (1986).

Examples of the water-miscible organic solvent (including a water-soluble organic solvent) which is preferably used in the present invention include alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, tert-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol), polyhydric alcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentanediol, glycerin, hexanetriol, thiodiglycol), glycol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether,

ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyethyleneimine, tetramethylpropylenediamine) and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, 2-pyrrolidone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 2-oxazolidone, 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone). These water-miscible organic solvents can be used in combination of two or more thereof. Among these, water-miscible organic solvents (preferably water-soluble organic solvents) having a boiling point of 150°C or more (preferably 200°C or more) are preferably used in the present invention.

Other components which can be contained in the ink composition for inkjet recording of the present invention are described below.

The inkjet recording ink (composition) of the present invention may contain a surfactant to control the liquid properties of the ink composition, whereby excellent effects can be provided, such as enhancement of the ejection stability of the ink composition, improvement of



water resistance of the image and prevention of bleeding of the printed ink composition.

Examples of the surfactant include anionic surfactants such as sodium dodecylsulfate, sodium dodecyloxysulfonate and sodium alkylbenzenesulfonate, cationic surfactants such as cetylpyridinium chloride, trimethylcetylammonium chloride and tetrabutylammonium chloride, and nonionic surfactants such as polyoxyethylene nonylphenyl ether, polyoxyethylene naphthyl ether and polyoxyethylene octylphenyl ether. Among these, nonionic surfactants are preferred.

The surfactant content is from 0.001 to 15 wt%, preferably from 0.005 to 10 wt%, more preferably from 0.01 to 5 wt%, based on the ink composition.

The inkjet recording ink of the present invention can be produced by dissolving or dispersing the dye in an aqueous medium. The "aqueous medium" as used in the present invention means water or a mixture of water and a slight amount of water-miscible organic solvent, where an additive such as wetting agent, stabilizer, antiseptic or defoaming agent is added, if desired.

In the case where the above-described dye is an oil-soluble dye, the ink can be prepared by dissolving the oil-soluble dye in a high boiling point organic solvent and emulsion-dispersing it in an aqueous medium.

The high boiling point organic solvent for use in the present invention has a boiling point of 150°C or more, preferably 170°C or more.

Examples thereof include phthalic acid esters (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl) isophthalate, bis(1,1-diethylpropyl) phthalate), esters of phosphoric acid or phosphone (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, dioctylbutyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridecyl phosphate, di-2-ethylhexylphenyl phosphate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecanamide, N,N-diethylaurylamide), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic esters (e.g., dibutoxyethyl succinate, di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, diethyl azelate, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins (e.g., paraffins having a chlorine content of 10 to 80%), trimesic acid esters (e.g., tributyl trimesate), dodecylbenzene, diisopropyl-naphthalene, phenols (e.g., 2,4-di-tert-amyl-

phenyl, 4-dodecyloxyphenol, 4-dodecyloxycarbonylphenol, 4-(4-dodecyloxyphenylsulfonyl)phenol), carboxylic acids (e.g., 2-(2,4-di-tert-amylphenoxy)butyric acid, 2-ethoxyoctanecanoic acid) and alkylphosphoric acids (e.g., di-(2-ethylhexyl)phosphoric acid and diphenylphosphoric acid).

These high boiling point organic solvents may be used individually or as a mixture of several kinds thereof (for example, tricresyl phosphate and dibutyl phthalate, trioctyl phosphate and di(2-ethylhexyl) sebacate, or dibutyl phthalate and poly(N-tert-butylacrylamide)).

Examples of the high boiling point organic solvent for use in the present invention, other than the above-described compounds, and/or the synthesis method of the high boiling point organic solvents are described, for example, in U.S. Patents 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321 and 5,013,639, EP-A-276319, EP-A-286253, EP-A-289820, EP-A-309158, EP-A-309159, EP-A-309160, EP-A-509311, EP-A-510576, East German Patents 147,009, 157,147, 159,573 and 225,240A, British Patent 2091124A, JP-A-48-47335, JP-A-50-26530, JP-A-51-

25133, JP-A-51-26036, JP-A-51-27921, JP-A-51-27922, JP-A-51-149028, JP-A-52-46816, JP-A-53-1520, JP-A-53-1521, JP-A-53-15127, JP-A-53-146622, JP-A-54-91325, JP-A-54-106228, JP-A-54-118246, JP-A-55-59464, JP-A-56-64333, JP-A-56-81836, JP-A-59-204041, JP-A-61-84641, JP-A-62-118345, JP-A-62-247364, JP-A-63-167357, JP-A-63-214744, JP-A-63-301941, JP-A-64-9452, JP-A-64-9454, JP-A-64-68745, JP-A-1-101543, JP-A-1-102454, JP-A-2-792, JP-A-2-4239, JP-A-2-43541, JP-A-4-29237, JP-A-4-30165, JP-A-4-232946 and JP-A-4-346338.

The high boiling point organic solvent is used in an amount of from 0.01 to 3.0 times, preferably from 0.01 to 1.0 time in terms of the weight ratio to the oil-soluble dye.

In the present invention, the oil-soluble dye or high boiling point organic solvent is used by emulsion-dispersing it in an aqueous medium. Depending on the case, a low boiling point organic solvent may also be used at the emulsion-dispersion in view of emulsifiability. The low boiling point organic solvent is an organic solvent having a boiling point of about 30 to 150°C at atmospheric pressure. Preferred examples thereof include esters (e.g., ethyl acetate, butyl acetate, ethyl propionate,  $\beta$ -ethoxyethyl acetate, methylcellosolve acetate), alcohols (e.g., isopropyl alcohol, n-butyl alcohol, secondary butyl alcohol), ketones (e.g., methyl isobutyl ketone, methyl

ethyl ketone, cyclohexanone), amides (e.g., dimethylformamide, N-methylpyrrolidone) and ethers (e.g., tetrahydrofuran, dioxane), however, the present invention is not limited thereto.

In the emulsion-dispersion, an oil phase obtained by dissolving the dye in a high boiling organic solvent or depending on the case, in a mixed solvent of a high boiling organic solvent and a low boiling organic solvent is dispersed in an aqueous phase mainly comprising water to form fine oil droplets of the oil phase. At this time, in either one or both of the aqueous phase and the oil phase, additives described later, such as surfactant, wetting agent, dye stabilizer, emulsification stabilizer, antiseptic and fungicide, can be added, if desired.

In a conventional emulsification method, an oil phase is added to an aqueous phase, however, a so-called phase inversion emulsification method of adding dropwise an aqueous phase in an oil phase can also be preferably used.

In performing the emulsion-dispersion of the present invention, various surfactants can be used. Preferred examples thereof include anionic surfactants such as fatty acid salt, alkylsulfuric ester salt, alkylbenzenesulfonate, alkylnaphthalenesulfonate, dialkylsulfosuccinate, alkylphosphoric ester salt, naphthalenesulfonic acid formalin condensate and polyoxyethylene alkylsulfuric ester salt,

and nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine, glycerin fatty acid ester and oxyethylene oxypropylene block copolymer. Also, SURFYNOLS (produced by Air Products & Chemicals), which are an acetylene-base polyoxyethylene oxide surfactant, are preferably used. Furthermore, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. In addition, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can also be used.

For the purpose of stabilizing the dispersion immediately after the emulsification, a water-soluble polymer may be added in combination with the surfactant. Preferred examples of the water-soluble polymer include polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, polyacrylic acid, polyacrylamide and copolymers thereof. Also, natural water-soluble polymers such as polysaccharides, casein and gelatin are also preferably used. Furthermore, for the stabilization of the dye dispersion, a polymer which does not substantially dissolve in an aqueous medium, such as polyvinyl, polyurethane, polyester, polyamide, polyurea and polycarbonate obtained

by the polymerization of acrylic acid esters, methacrylic acid esters, vinyl esters, acrylamides, methacrylamides, olefins, styrenes, vinyl ethers or acrylonitriles, can also be used in combination. The polymer preferably contains  $\text{-SO}_3^-$  or  $\text{-COO}^-$ . In the case of using such a polymer which does not substantially dissolve in an aqueous medium, the polymer is preferably used in an amount of 20 wt% or less, more preferably 10 wt% or less, based on the high boiling point organic solvent.

In preparing an aqueous ink composition by dispersing the oil-soluble dye or high boiling point organic solvent according to emulsion-dispersion, control of the particle size is particularly important. In order to improve the color purity or density of an image formed by the inkjet recording, it is essential to reduce the average particle size. The average particle size is preferably 1  $\mu\text{m}$  or less, more preferably from 5 to 100 nm in terms of the volume average particle size.

The volume average particle size and particle size distribution of the dispersed particles can be easily measured by a known method such as static light scattering method, dynamic light scattering method, centrifugal precipitation method and the method described in Jikken Kagaku Koza (Lecture of Experimental Chemistry), 4th ed., pp. 417-418. For example, the ink composition is diluted

with distilled water to have a particle concentration of 0.1 to 1 wt%, then, the particle size can be easily measured by a commercially available volume average particle size measuring apparatus (for example, Microtrac UPA, manufactured by Nikkiso K.K.). The dynamic light scattering method utilizing the laser Doppler effect is particularly preferred because even a small particle size can be measured.

The volume average particle size is an average particle size weighted with the particle volume and it is obtained by multiplying the diameter of individual particles with the volume of the particle and dividing the sum total of the obtained values by the total volume of the particles. The volume average particle size is described in Soichi Muroi, Kobunshi Latex no Kagaku (Chemistry of Polymer Latex), page 119, Kobunshikankokai Co., Ltd.

Also, it is revealed that the presence of coarse particles greatly affects the printing performance. More specifically, the coarse particle clogs the nozzle of head or even if the nozzle is not clogged, forms a soil to bring about failure or twist in the ejection of ink, whereby the printing performance is seriously affected. In order to prevent these troubles, it is important to reduce the number of particles having a particle size of 5  $\mu\text{m}$  or more to 10 or less and the number of particles having a particle



size of 1  $\mu\text{m}$  or more to 1,000 or less, in 1  $\mu\text{l}$  of ink prepared.

For removing the coarse particles, a known method such as centrifugal separation or microfiltration can be used. The separation step may be performed immediately after the emulsion-dispersion or may be performed immediately before filling the ink in an ink cartridge after various additives such as wetting agent and surfactant are added to the emulsified dispersion.

A mechanically emulsifying apparatus is effective for reducing the average particle size and eliminating coarse particles.

As for the emulsifying apparatus, known apparatuses such as simple stirrer, impeller stirring system, in-line stirring system, mill system (e.g., colloid mill) and ultrasonic system can be used, however, a high-pressure homogenizer is particularly preferred.

The mechanism of the high-pressure homogenizer is described in detail in U.S. Patent 4,533,254 and JP-A-6-47264. Examples of the commercially available apparatus include Gaulin Homogenizer (manufactured by A.P. V Gaulin Inc.), Microfluidizer (manufactured by Microfluidex Inc.) and Altimizer (produced by Sugino Machine).

The high-pressure homogenizer with a mechanism of pulverizing particles in an ultrahigh pressure jet stream

recently described in U.S. Patent 5,720,551 is particularly effective for the emulsion-dispersion of the present invention. Examples of the emulsifying apparatus using this ultrahigh pressure jet stream include DeBEE2000 (manufactured by BEE International Ltd.).

In performing the emulsification by a high-pressure emulsion-dispersing apparatus, the pressure is 50 MPa or more, preferably 60 MPa or more, more preferably 180 MPa or more.

A method of using two or more emulsifying apparatuses, for example, by performing the emulsification in a stirring emulsifier and then passing the emulsified product through a high-pressure homogenizer is particularly preferred. Also, a method of once performing the emulsion-dispersion by such an emulsifying apparatus, adding an additive such as wetting agent or surfactant, and then again passing the dispersion through a high-pressure homogenizer before filling the ink into a cartridge is preferred.

In the case of containing a low boiling point organic solvent in addition to the high boiling point organic solvent, the low boiling point solvent is preferably removed in view of stability of the emulsified product, safety and hygiene. For removing the low boiling point solvent, various known methods can be used according to the kind of the solvent. Examples of the method include

evaporation, vacuum evaporation and ultrafiltration. The removal of the low boiling point organic solvent is preferably performed as soon as possible immediately after the emulsification.

In the ink composition for inkjet recording according to the present invention, additives such as drying inhibitor for preventing clogging due to drying of ink at the ejection port, permeation accelerator for attaining more successful permeation of ink into paper, ultraviolet absorbent, antioxidant, viscosity adjusting agent, surface tension adjusting agent, dispersant, dispersion stabilizer, fungicide, rust inhibitor and pH adjusting agent, can be appropriately selected and used in an appropriate amount.

The drying inhibitor for use in the present invention is preferably a water-soluble organic solvent having a vapor pressure lower than water. Specific examples thereof include polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, thiodiglycol, dithiodiglycol, 2-methyl-1,3-propanediol, 1,2,6-hexanetriol, acetylene glycol derivative, glycerin and trimethylolpropane; lower alkyl ethers of polyhydric alcohol, such as ethylene glycol monomethyl(or ethyl) ether, diethylene glycol monomethyl(or ethyl) ether and triethylene glycol monoethyl(or butyl) ether; heterocyclic compounds such as 2-pyrrolidone, N-methyl-2-pyrrolidone,

1,3-dimethyl-2-imidazolidinone and N-ethylmorpholine; sulfur-containing compounds such as sulfolane, dimethylsulfoxide and 3-sulfolene; polyfunctional compounds such as diacetone alcohol and diethanolamine; and urea derivatives. Among these, polyhydric alcohols such as glycerin and diethylene glycol are preferred. The drying inhibitors may be used individually or in combination of two or more thereof. The drying inhibitor is preferably contained in an amount of 10 to 50 wt% in the ink.

Examples of the permeation accelerator which can be used in the present invention include alcohols such as ethanol, isopropanol, butanol, di(tri)ethylene glycol monobutyl ether and 1,2-hexanediol, sodium laurylsulfate, sodium oleate and nonionic surfactants. A sufficiently high effect can be obtained by adding from 10 to 30 wt% of the permeation accelerator in the ink. The permeation accelerator is preferably used in an amount of causing no bleeding of printed letter or no print through.

Examples of the ultraviolet absorbent which can be used in the present invention for improving the preservability of image include benzotriazole-base compounds described in JP-A-58-185677, JP-A-61-190537, JP-A-2-782, JP-A-5-197075 and JP-A-9-34057, benzophenone-base compounds described in JP-A-46-2784, JP-A-5-194483 and U.S. Patent 3,214,463, cinnamic acid-base compounds described in JP-B-

48-30492 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-B-56-21141 and JP-A-10-88106, triazine-base compounds described in JP-A-4-298503, JP-A-8-53427, JP-A-8-239368, JP-A-10-182621 and JP-T-8-501291 (the term "JP-T" as used herein means a "published Japanese translation of a PCT patent application"), compounds described in Research Disclosure No. 24239, and compounds of absorbing ultraviolet light and emitting fluorescent light, so-called fluorescent brightening agents, represented by stilbene-base compounds and benzoxazole-base compounds.

As the antioxidant which can be used in the present invention for improving the preservability of image, various organic or metal complex discoloration inhibitors can be used. Examples of the organic discoloration inhibitor include hydroquinones, alkoxyphenols, dialkoxyphenols, phenols, anilines, amines, indanes, chromans, alkoxyanilines and heterocyclic compounds. Examples of the metal complex include nickel complex and zinc complex. More specifically, compounds described in patents cited in Research Disclosure, Nos. 17643 (Items VII-I to VII-J), 15162, 18716 (page 650, left column), 36544 (page 527), 307105 (page 872) and 15162, and compounds included in formulae of representative compounds and specific examples thereof described in JP-A-62-215272

(pages 127 to 137) can be used.

Examples of the fungicide for use in the present invention include sodium dehydroacetate, sodium benzoate, sodium pyridinethione-1-oxide, ethyl p-hydroxybenzoate, 1,2-benzisothiazolin-3-one and salts thereof. The fungicide is preferably used in an amount of 0.02 to 5.00 wt% in the ink.

The fungicides are described in detail in Bokin Bobai Zai Jiten (Dictionary of Microbicide and Fungicide), compiled by Nippon Bokin Bobai Gakkai Jiten Henshu Iinkai.

Examples of the rust inhibitor include acidic sulfite, sodium thiosulfate, ammon thioglycolate, diisopropyl-ammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite and benzotriazole. The rust inhibitor is preferably used in an amount of 0.02 to 5.00 wt% in the ink.

The pH adjusting agent for use in the present invention can be suitably used for adjusting the pH and imparting dispersion stability. The pH of the ink is preferably adjusted to 8 to 11 at 25°C. When the pH is less than 8, the solubility of dye decreases to readily cause clogging of a nozzle, whereas when it exceeds 11, the water resistance is liable to deteriorate. Examples of the pH adjusting agent include organic bases and inorganic alkalis for basic compounds, and organic acids and

inorganic acids for acidic compounds.

Examples of the organic base include triethanolamine, diethanolamine, N-methyldiethanolamine and dimethylethanolamine. Examples of the inorganic alkali include hydroxides of alkali metal (e.g., sodium hydroxide, lithium hydroxide, potassium hydroxide), carbonates of alkali metal (e.g., sodium carbonate, sodium hydrogencarbonate), and ammonium. Examples of the organic acid include acetic acid, propionic acid, trifluoroacetic acid and an alkylsulfonic acid. Examples of the inorganic acid include hydrochloric acid, sulfuric acid and phosphoric acid.

In the present invention, apart from the above-described surfactants, a nonionic, cationic or anionic surfactant is used as the surface tension adjusting agent. Examples thereof include anionic surfactants such as fatty acid salt, alkylsulfuric ester salt, alkylbenzenesulfonate, alkyl-naphthalenesulfonate, dialkylsulfosuccinate, alkylphosphoric ester salt, naphthalenesulfonic acid formalin condensate and polyoxyethylenealkylsulfuric ester salt, and nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylaryl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine, glycerin fatty acid ester and oxyethylene oxypropylene block copolymer. Also, SURFYNOLS (produced by

Air Products & Chemicals), which are an acetylene-base polyoxyethylene oxide surfactant, are preferably used. Also, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. In addition, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can also be used.

The surface tension of the ink for use in the present invention is, irrespective of dynamic surface tension or static surface tension, preferably from 20 to 50 mN/m, more preferably from 20 to 40 mN/m, at 25°C. When the surface tension exceeds 50 mN/m, ejection stability and printing quality, for example, bleeding due to color mixing or occurrence of feathering, are seriously deteriorated, whereas when the surface tension of the ink is less than 20 mN/m, printing failure may occur due to, for example, attachment of ink to the surface at the ejection.

The ink of the present invention preferably has a viscosity at 25°C of 1 to 20 mPa·s, more preferably from 2 to 15 mPa·s, still more preferably from 2 to 10 mPa·s. When the viscosity exceeds 20 mPa·s, the fixing rate of the recorded image decreases and the ejection performance also decreases, whereas when it is less than 1 mPa·s, the bleeding occurs in the recorded image to decrease the grade.

The viscosity can be appropriately adjusted by the



amount of the ink solvent added. Examples of the ink solvent include glycerin, diethylene glycol, triethanolamine, 2-pyrrolidone, diethylene glycol monobutyl ether and triethylene glycol monobutyl ether.

A viscosity adjusting agent may also be used. Examples of the viscosity adjusting agent include water-soluble polymers such as celluloses or polyvinyl alcohol, and nonionic surfactants. The viscosity adjusting agent is described in detail in Nendo Chosei Gijutsu (Viscosity Adjusting Technology), Chap. 9, Gijutsu Joho Kyokai (1999), and Inkjet Printer Yo Chemicals (98 Zoho) -Zairyo no Kaihatsu Doko-Tenbo Chosa- (Chemicals for Inkjet Printer (Enlarged Edition of 98) -Survey on Tendency-Prospect of Development of Materials-), pp. 162-174, CMC Publishing Co., Ltd. (1997).

In the present invention, if desired, the above-described various cationic, anionic and nonionic surfactants can be used as the dispersant or dispersion stabilizer, and fluorine-base or silicone-base compounds, chelating agents represented by EDTA, and the like can be used as the defoaming agent.

In preparing the ink of the present invention, in the case of a water-soluble ink, the dye is preferably first dissolved in water and thereafter, various solvents and additives are added, dissolved and mixed to provide a

uniform ink solution.

For dissolving the dye, various methods such as stirring, ultrasonic irradiation and shaking can be used. Among these, stirring is preferred. In performing the stirring, various systems known in the field of art can be used, such as flow stirring and stirring utilizing the shearing force by means of a reversal agitator or a dissolver. Also, a stirring method utilizing the shearing force with the bottom surface of a vessel, such as magnetic stirrer, can be advantageously used.

The recording paper and recording film as reflective media for use in the image recording method of the present invention are described below. The support which can be used for the recording paper or film is produced, for example, from a chemical pulp such as LBKP and NBKP, a mechanical pulp such as GP, PGW, RMP, TMP, CTMP, CMP and CGP, or a waste paper pulp such as DIP, by mixing, if desired, conventionally known additives such as pigment, binder, sizing agent, fixing agent, cation agent and paper strength increasing agent, and then paper-making the mixture by using various machines such as Fourdrinier paper machine and cylinder paper machine. Further, synthetic paper or plastic film sheet may be used. The thickness of the support is preferably from 10 to 250  $\mu\text{m}$  and the basis weight is preferably from 10 to 250  $\text{g}/\text{m}^2$ .

An ink-receiving layer and a backcoat layer may be directly provided on the support to produce an image-receiving material, or after providing a size press or an anchor coat layer by using starch, polyvinyl alcohol or the like, an ink-receiving layer and a backcoat layer may be provided to produce an image-receiving material. The support may be further subjected to a planalizing treatment by a calendering device such as machine calender, TG calender and soft calender.

In the present invention, the support is preferably paper both surfaces of which are laminated with polyolefin (for example, polyethylene, polystyrene, polybutene or a copolymer thereof) or polyethylene terephthalate, or a plastic film. In the polyolefin, a white pigment (for example, titanium oxide or zinc oxide) or a tinting dye (for example, cobalt blue, ultramarine or neodymium oxide) is preferably added.

The ink-receiving layer provided on the support contains a porous material or an aqueous binder. Also, the ink-receiving layer preferably contains a pigment and the pigment is preferably a white pigment. Examples of the white pigment include inorganic white pigments such as calcium carbonate, kaolin, talc, clay, diatomaceous earth, synthetic amorphous silica, aluminum silicate, magnesium silicate, calcium silicate, aluminum hydroxide, alumina,

lithopone, zeolite, barium sulfate, calcium sulfate, titanium dioxide, zinc sulfide and zinc carbonate, and organic pigments such as styrene-base pigment, acryl-base pigment, urea resin and melamine resin. Among these, porous inorganic white pigments are preferred, and synthetic amorphous silica and the like having a large pore area are more preferred. The synthetic amorphous silica may be either a silicic acid anhydride obtained by a dry production process or a silicic acid hydrate obtained by a wet production process, but a silicic acid hydrate is preferred. These pigments may be used in combination of two or more thereof.

Examples of the aqueous binder contained in the ink-receiving layer include water-soluble polymers such as polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinylpyrrolidone, polyalkylene oxide and polyalkylene oxide derivatives, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. These aqueous binders may be used individually or in combination of two or more thereof. Among these, polyvinyl alcohol and silanol-modified polyvinyl alcohol are preferred in the present invention in view of adhesion to the pigment and peeling resistance of the ink-receiving layer.

The ink-receiving layer may contain a mordant, a water-proofing agent, a light fastness enhancer, a surfactant, a hardening agent and other additives in addition to the pigment and the aqueous binder.

The mordant added to the ink-receiving layer is preferably immobilized and for such a purpose, a polymer mordant is preferably used.

The polymer mordant is described in JP-A-48-28325, JP-A-54-74430, JP-A-54-124726, JP-A-55-22766, JP-A-55-142339, JP-A-60-23850, JP-A-60-23851, JP-A-60-23852, JP-A-60-23853, JP-A-60-57836, JP-A-60-60643, JP-A-60-118834, JP-A-60-122940, JP-A-60-122941, JP-A-60-122942, JP-A-60-235134, JP-A-1-161236 and U.S. Patents 2,484,430, 2,548,564, 3,148,061, 3,309,690, 4,115,124, 4,124,386, 4,193,800, 4,273,853, 4,282,305 and 4,450,224. An image-receiving material containing the polymer mordant described in JP-A-1-161236 (pages 212 to 215) is particularly preferred. When the polymer mordant described in JP-A-1-161236 is used, an image having excellent image quality can be obtained and at the same time, the light fastness of the image is improved.

The water-proofing agent is effective for obtaining a water-resistant image. The water-proofing agent is preferably a cationic resin. Examples of the cationic resin include polyamidopolyamine epichlorohydrin,

polyethyleneimine, polyaminesulfone, poly-dimethyldiallyl-ammonium chloride, cation polyacrylamide and colloidal silica. Among these cationic resins, polyamidopolyamine epichlorohydrin is preferred. The content of the cationic resin is preferably from 1 to 15 wt%, more preferably from 3 to 10 wt%, based on the entire solid content of the ink-receiving layer.

Examples of the light fastness enhancer include zinc sulfate, zinc oxide, hindered amine-base antioxidants, and benzotriazole-base ultraviolet absorbents such as benzophenone. Among these, zinc sulfate is preferred.

The surfactant functions as a coating aid, an adherence improver, a slipperiness improver or an antistatic agent. The surfactant is described in JP-A-62-173463 and JP-A-62-183457.

In place of the surfactant, an organic fluoro compound may be used. The organic fluoro compound is preferably hydrophobic. Examples of the organic fluoro compound include fluorine-containing surfactants, oily fluorine-base compounds (for example, fluorine oil) and solid fluorine compound resins (for example, ethylene tetrafluoride resin). The organic fluoro compound is described in JP-B-57-9053 (columns 8 to 17), JP-A-61-20994 and JP-A-62-135826.

As the hardening agent, for example, the materials

described in JP-A-1-161236 (page 222) can be used.

Other examples of the additive added to the ink-receiving layer include a pigment dispersant, a thickener, a defoaming agent, a dye, a fluorescent brightening agent, an antiseptic, a pH adjusting agent and a matting agent. The ink-receiving layer may be composed of one layer or two layers.

In the recording paper or film, a backcoat layer may also be provided. Examples of the component which can be added to this layer include a white pigment, an aqueous binder and other components.

Examples of the white pigment contained in the backcoat layer include inorganic white pigments such as precipitated calcium carbonate light, ground calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminum hydroxide, alumina, lithopone, zeolite, hydrated halloysite, magnesium carbonate and magnesium hydroxide, and organic pigments such as styrene-base plastic pigment, acryl-base plastic pigment, polyethylene, microcapsule, urea resin and melamine resin.

Examples of the aqueous binder contained in the

backcoat layer include water-soluble polymers such as styrene/maleate copolymer, styrene/acrylate copolymer, polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose and polyvinylpyrrolidone, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. Other components contained in the backcoat layer include a defoaming agent, a foam inhibitor, a dye, a fluorescent brightening agent, an antiseptic and a water-proofing agent.

In a constituent layer (including the back layer) of the inkjet recording paper or film, a polymer fine particle dispersion may be added. The polymer fine particle dispersion is used for the purpose of improving film properties, for example, stabilizing dimension and preventing curling, adhesion or film cracking. The polymer fine particle dispersion is described in JP-A-62-245258, JP-A-62-1316648 and JP-A-62-110066. When a polymer fine particle dispersion having a low glass transition temperature (40°C or less) is added to a layer containing a mordant, the layer can be prevented from cracking or curling. The curling can be prevented also by adding a polymer fine particle dispersion having a high glass transition temperature to the back layer.

The present invention is not limited in the inkjet



recording system and is used for a known system, for example, an electric charge controlling system of ejecting the ink by utilizing the electrostatic induction force, a drop-on-demand system (pressure pulse system) utilizing an oscillation pressure of a piezoelectric element, an acoustic inkjet system wherein electric signals are converted into acoustic beams, and the ink is irradiated with the beam to eject the ink using the radiation pressure, and a thermal inkjet (bubble jet) system of heating the ink to form a bubble and ejecting the ink utilizing the generated pressure.

The inkjet recording system includes a system of ejecting a large number of small-volume ink droplets of a so-called photo ink having a low concentration, a system of improving the image quality by using a plurality of inks having substantially the same color hue but different in the concentration, and a system using a colorless transparent ink.

The inkjet recording ink set of the present invention can be used for the uses other than the inkjet recording, such as a material for display image, an image-forming material for interior decoration and an image-forming material for outdoor decoration.

Examples of the material for display image include various materials such as poster, wall paper, ornamental

articles (e.g., decorative figurine, doll), handbill for commercial advertisement, wrapping paper, wrapping material, paper bag, vinyl bag, package material, billboard, image drawn on or attached to the side surface of transportation facilities (e.g., automobile, bus, electric car), and clothing with a logo. In the case of using the ink of the present invention as a material for forming a display image, the image includes not only a narrow definition of image but also all patterns by an ink, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

Examples of the material for interior decoration include various materials such as wallpaper, ornamental articles (e.g., decorative figurine, doll), luminaire member, furniture member and design member of floor or ceiling. In the case of using the ink of the present invention as a material for forming an image, the image includes not only a narrow definition of image but also all patterns by an ink, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

Examples of the material for outdoor decoration include various materials such as wall material, roofing material, billboard, gardening material, outdoor ornamental articles (e.g., decorative figurine, doll) and outdoor luminaire member. In the case of using the ink of the

present invention as a material for forming an image, the image includes not only a narrow definition of image but also all patterns by an ink, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

In these uses, examples of the medium on which the pattern is formed include various materials such as paper, fiber, cloth (including non-woven fabric), plastic, metal and ceramic. Examples of the dyeing form include mordanting, printing and fixing of a dye in the form of a reactive dye having introduced therein a reactive group. Among these, preferred is dyeing by mordanting.

The present invention is described below by referring to Examples, however, the present invention is not limited thereto.

#### Example 1

Deionized water was added to the following components to make 1 liter and the mixture was stirred for 1 hour under heating at 30 to 40°C, followed by adjusting the pH thereof to 9 by 10 mol/liter of KOH. Then, the solution was filtered under reduced pressure through a microfilter having an average pore size of 0.25  $\mu\text{m}$  to prepare Light Magenta Ink.

Magenta Dye (a-36)	8.2 g/liter
Diethylene glycol	60 g/liter

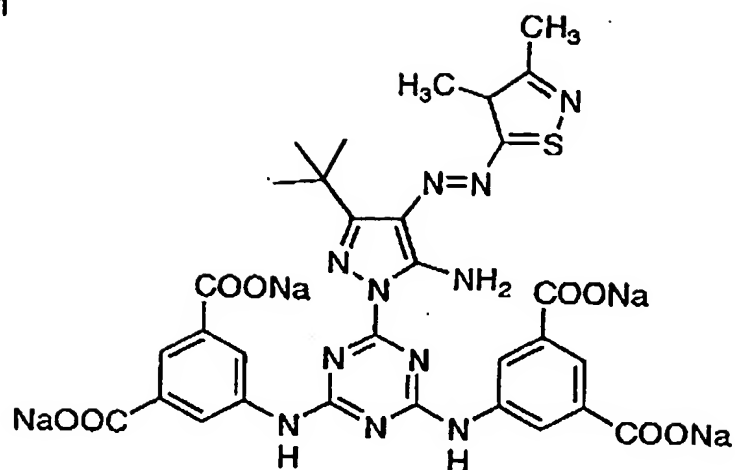
Urea	4 g/liter
Glycerin	170 g/liter
Triethylene glycol monobutyl ether (TEGmBE)	110 g/liter
2-Pyrrolidone	30 g/liter
Triethanolamine	3 g/liter
Benzotriazole	0.02 g/liter
BROXEL XL2	1 g/liter
Surfactant (W-1)	20 g/liter

Furthermore, Magenta Ink, Light Cyan Ink, Cyan Ink, Yellow Ink, Dark Yellow Ink and Black Ink were prepared by changing the dye and additives, whereby Ink Set 101 shown in Table 1 below was produced.

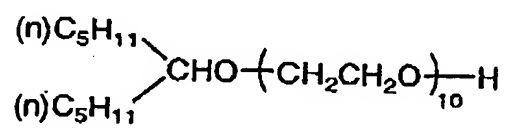
Table 1

	Light Cyan	Cyan	Light Magenta	Magenta	Yellow	Dark Yellow	Black
Dye (g/liter)	No. 154 15.0	No. 154 55.0	a-36 8.2	a-36 24.4	Y-1 55.0	Y-1 64.0	B-1 70.0
						No. 154 14	B-2 5.0
						a-36 23	Y-1 20.0
Diethylene glycol (g/liter)	100	80	60	76	100	40	20
Urea (g/liter)	2	4	4	4	-	7	-
Glycerin (g/liter)	100	90	170	150	100	100	110
Triethylene glycol monobutyl ether (g/liter)	110	110	110	107	110	110	-
Diethylene glycol monobutyl ether	-	-	-	-	-	-	110
2-Pyrrolidone (g/liter)	-	30	30	-	-	40	40
Triethanolamine (g/liter)	6	6	3	3	1	1	10
Benzotriazole (g/liter)	0.02	0.02	0.02	0.02	0.03	0.03	0.03
Proxel	1.5	1.5	1	1	2	2	2
Surfactant XL2 (g/liter)	15	15	20	20	10	10	15
Surfactant W-1 (g/liter)							
Deionized water was added to make 1 liter.							

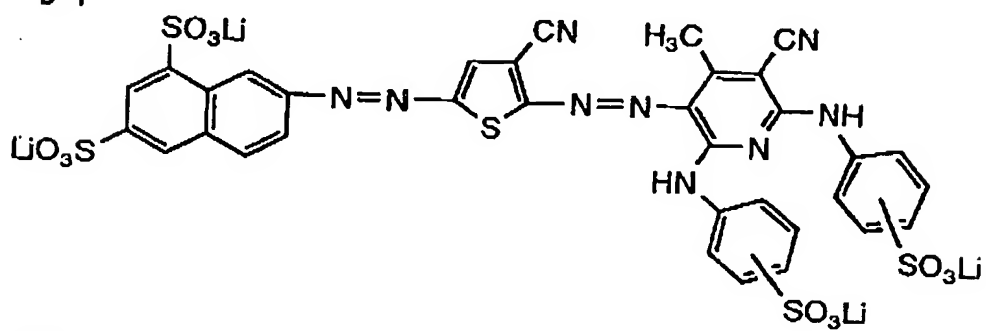
Y-1



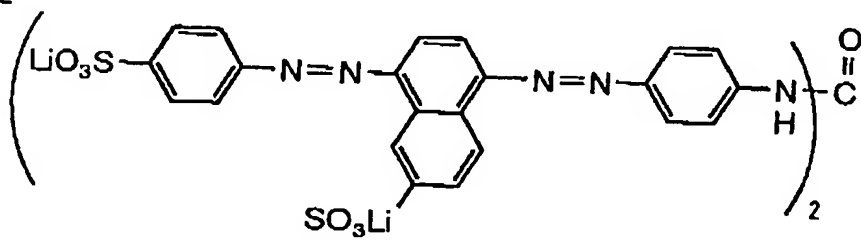
W-1



B-1



B-2



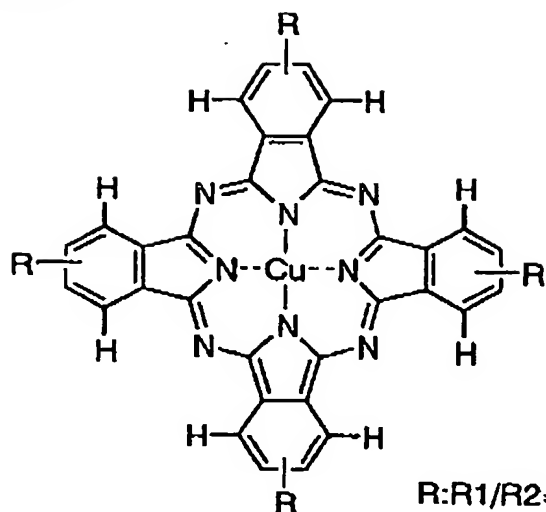
Ink Sets 102 to 105 were produced by changing the dyes in Ink Set 101 as shown in Table 2. In the Table, the cation is denoted in the parenthesis.

Table 2

Ink Set	Light Cyan, Cyan Dye	Light Magenta, Magenta Dye	Yellow Dye	Dark Yellow Dye	Black Dye	Remarks
101	No. 154 (Li)	a-36 (Na)	Y-1 (Na)	Y-1 (Na) No. 154 (Li) a-36 (Na)	B-1 (Li) B-2 (Li) Y-1 (Na)	Invention
102	EXC-1 (Li)	a-36 (Na)	EXY-1 (Na)	EXY-1 (Na) EXC-1 (Li) a-36 (Na)	EXB-1 (Li) B-2 (Li) EXY-1 (Na)	Comparison
103	EXC-2 (K)	a-36 (Na)	Y-1 (Na)	EXY-1 (Na) EXC-2 (K) a-36 (Na)	EXB-2 (Li) B-2 (Li) Y-1 (Na)	Comparison
104	C-2 (Li)	a-36 (Na)	Y-2 (Na)	Y-2 (Na) No. 154 (Li) a-36 (Na)	B-3 (Li) B-2 (Li) Y-2 (Li)	Invention
105	C-2 (Li)	a-36 (Na)	Y-3 (Na)	Y-3 (Na) No. 154 (Li) a-36 (Na)	B-4 (Li) B-2 (Li) Y-3 (Na)	Invention



EXC-1

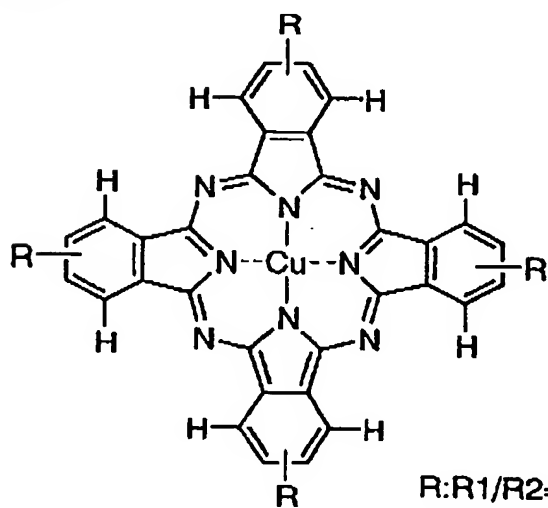


R:R1/R2=2/2

R1=SO<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Li

R2=SO<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SO<sub>2</sub>NHCH<sub>2</sub>CH(OH)CH<sub>3</sub>

EXC-2

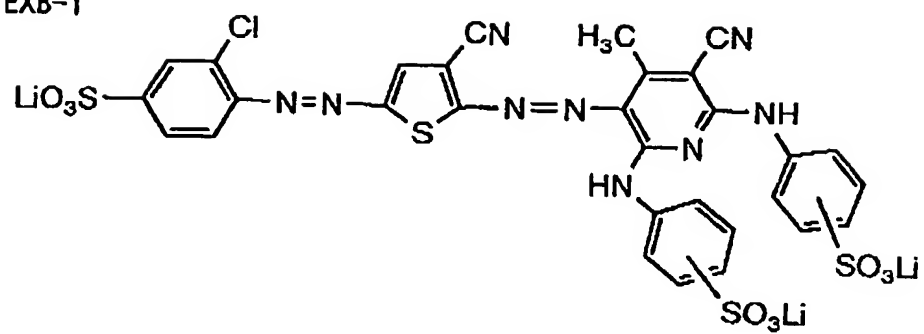


R:R1/R2=3/1

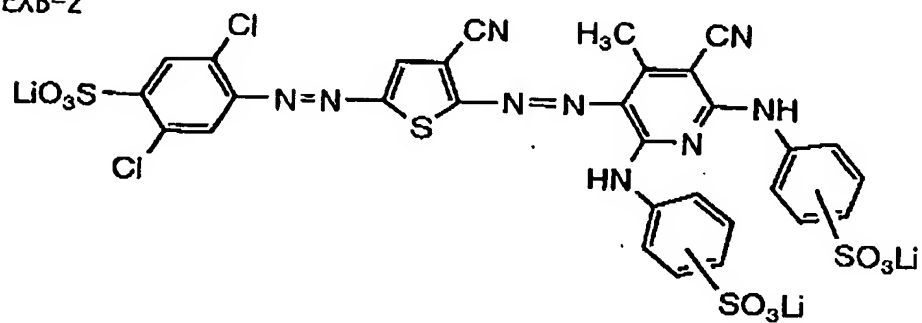
R1=SO<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>K

R2=SO<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SO<sub>2</sub>NHCH<sub>2</sub>CH(OH)CH<sub>3</sub>

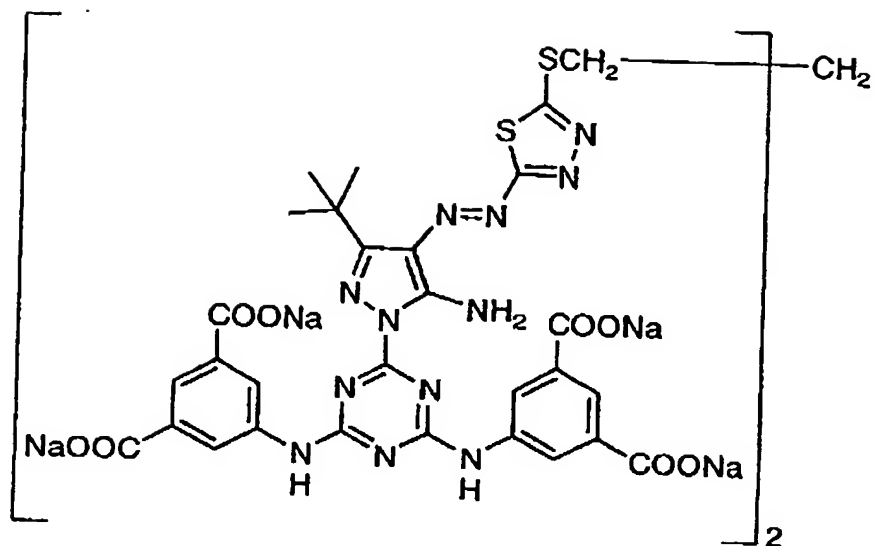
EXB-1



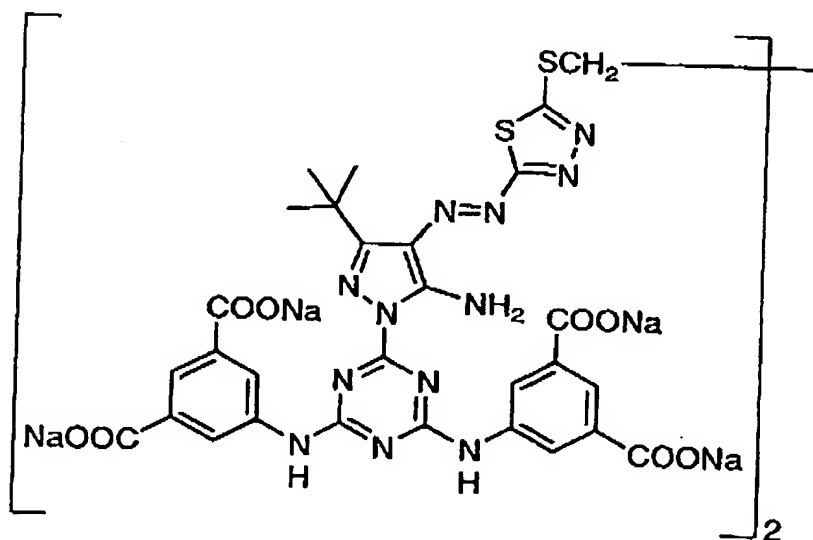
EXB-2



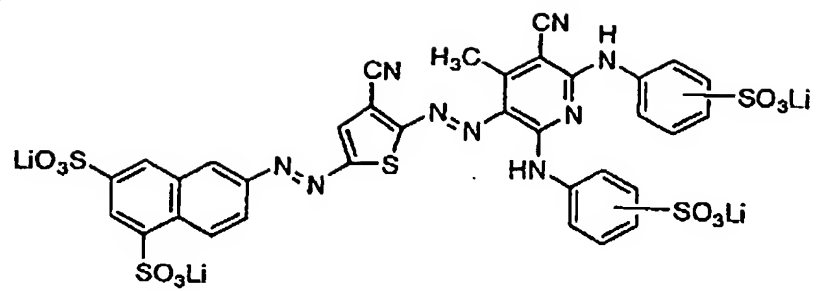
Y-2



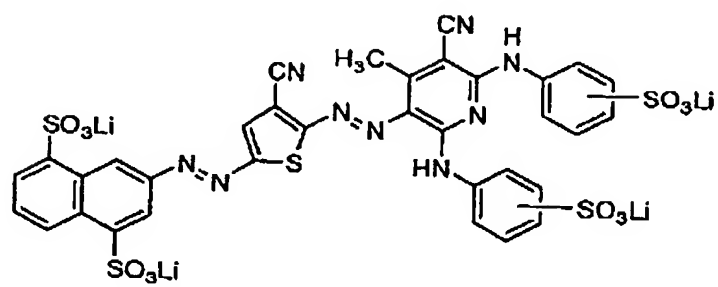
Y-3



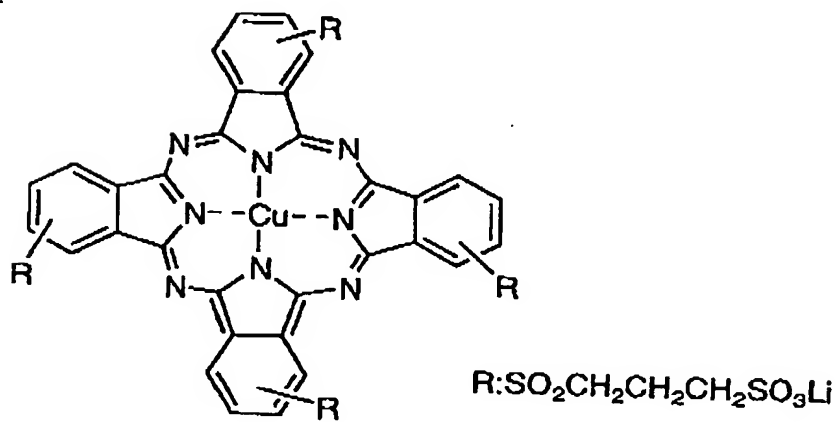
B-4



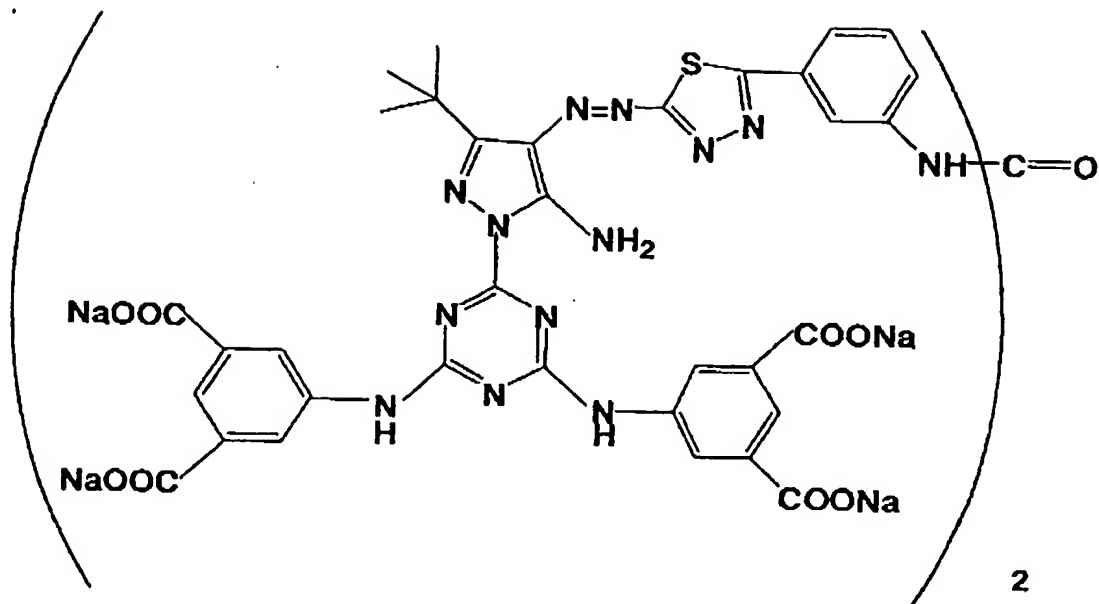
B-3



C-2



EXY-1



1) The inks of respective colors were simultaneously mixed at room temperature. Then, 0.2 ml of the mixed ink was dropped on glass-made Sekisui Microscope Plate UR-157 (produced by Sekisui Chemical Co., Ltd.) and after allowing it to stand at 25°C and 50% RH for 3 days, the presence or absence of precipitation was observed through a microscope. The results are shown in Table 3.

Subsequently, Ink Sets 101 to 105 each was filled in cartridges of inkjet printer PM920C (manufactured by Seiko Epson Corporation) and using the printer an image was printed on Epson PM Photographic Image-Receiving Paper produced by Seiko Epson Corporation. The image obtained

was subjected to the following evaluations.

## 2) Printing Performance

The cartridges were set in the printer and after confirming that the inks were ejected through all nozzles, a solid image printed sample was prepared in an environment of 30°C and 80% RH and after allowing the sample to stand overnight under the same conditions, [1] evaluation of bronzing (surface metal gloss) and [2] measurement of reflection density  $C_i$  by X-Rite 310TR were performed. The results are shown in Table 4.

Table 3

Ink Set	Precipitation of blue color, cyan ink + magenta ink	Precipitation of green color, cyan ink + yellow ink	Precipitation of red color, magenta ink + yellow ink	Precipitation of black ink + dark yellow ink	Remarks
101	none	none	none	none	Invention
102	precipitated	none	none	precipitated	Comparison
103	precipitated	none	none	precipitated	Comparison
104	none	none	none	none	Invention
105	none	none	none	none	Invention

Table 4

Ink set	Generation of Bronzing in Blue Solid Area	R Density in Blue Solid Area	R Density in Green Solid Area	R Density in Red Solid Area	V Density in Black Solid Area	Remarks
101	none	2.15	2.17	1.65	2.55	Invention

102	generated	1.90	2.16	1.65	2.23	Comparison
103	generated	1.95	2.17	1.63	2.20	Comparison
104	none	2.17	2.18	1.67	2.60	Invention
105	none	2.16	2.18	1.66	2.63	Invention

It is seen that when the ink set of the present invention is used, precipitation of dye does not occur in the ink, the bronzing is less generated and high density is exhibited.

The oxidation potential (measured by the method described above in regard to the oxidation potential) of each dye used in Example 1 is shown in the parenthesis: No. 154 (1.11), a-36 (1.35), Y-1 (1.03), B-1 (1.3), B-2 (1.31), C-2 (1.1), Y-2 (1.02), Y-3 (1.03), B-3 (1.3), B-4 (1.3), EXC-1 (1.12), EXC-2 (1.13), EXY-1 (1.02), EXB-1 (1.3) and EXB-2 (1.3).

In any of dyes No. 154, a-36, Y-1, B-1, B-2, C-2, Y-2, Y-3, B-3 and B-4 used in Example 1, the total amount of cations other than the cations shown in Table 2 was 0.5 wt% or less in the ink.

As for the weather resistance of ink, particularly, light fastness and ozone fastness, a cyan image was tested under the following conditions and various performances were evaluated.

1) In the light fastness test where the image on Epson PM Photographic Image-Receiving Paper allowed to

stand without UV filter under Xe light of 87,000 lx [cd.sr/m<sup>2</sup>] for 3 days, the residual color ratio was 90% or more in all of Ink Sets 101 to 105.

2) In the monochromatic portion printed by using a monochrome (cyan) ink to give a cyan reflection density of 0.9 to 1.1 in a Status A filter, when stored in an ozone environment of 5 ppm for 24 hours, the dye residual ratio (density after discoloration/initial density  $\times$  100) after the storage was 80% or more in all of Ink Sets 101 to 105.

3) After the ozone discoloration under the conditions of 2, the amount of Cu ion flowed out into water was measured and found to be 20% or less of the cyan dye in all of Ink Sets 101 to 105.

When the image-receiving paper used in the present invention was changed to Inkjet Paper Photo Gloss Paper EX produced by Fuji Photo Film Co., Ltd. or PR101 produced by Canon Inc., the same effects as in the results above were confirmed.

#### Example 2

The same inks as prepared in Example 1 were filled in cartridges of Inkjet Printer BJ-F850 (manufactured by Canon Inc.) and using the printer an image was printed on Inkjet Paper Photo Gloss Paper EX produced by Fuji Photo Film Co., Ltd. and evaluated in the same manner as in Example 1. The same results as in Example 1 were obtained. When the



image-receiving paper was changed to Epson PM Photographic Image-Receiving Paper produced by Seiko Epson Corporation or PR101 produced by Canon Inc., the same effects were confirmed.

The entire disclosure of each and every foreign patent application from which the benefit of foreign priority has been claimed in the present application is incorporated herein by reference, as if fully set forth herein.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.